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TRANSLATION

THEORY OF EXPLOSIVES

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE
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EDITED MACHINE TRANSLATION

THEORY OF EXPLOSIVES

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PREPARED BY:

TRANSLATION DIVISION
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WP-AFB, OHIO.

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TEORIYA VZRYVCHATYKH VESHCHESTV

Sbornik Stateye

K. K. Andreyev, A. F. Belyayev, A. I. Gol'binder
and A. G. Gorst

Gosudarstvennoye
Nauchno-Tekhnicheskoye Izdatel'stvo

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Moskva - 1963

Pages 3-579

TABLE OF CONTENTS

THEORY OF EXPLOSIVES (Collection of Articles)

Edited by

K. K. Andreyev, A. F. Belyayev, A. I. Gol'binder and A. G. Gorst

State Scientific-technical Publishing House (State
Publishing House of the Defense Industry), Moscow 1963

The collection consists of four divisions. ~~In~~ the first division we covers the questions of sensitivity of explosives to mechanical influences, considered on the basis of new presentations about the appearance of an explosion during shock. Articles in the second division are devoted to the results of the investigation of the thermal disintegration of different nitro esters and certain nitrocompounds. In the third division there is research on the ignition and detonation of explosives. In the fourth division are articles refering to different questions of the theory of explosives( )The collection is intended for workers of scientific research institutes, design bureaus, and enterprises involved in the production and application of explosives, and also for teachers, post-graduates, and senior students of technical colleges of corresponding specialties.

Preface

The absence of a magazine, devoted to explosives, hampers and delays the possibility of familiarization of specialists with the results of research in theoretical problems of ignition, detonation, and slow disintegration. In a certain measure this difficulty is compensated by the publication of collections of articles on the theory of explosives. The first of them was issued by Oborongiz in 1940, the second -- ("Problems of the Theory of Explosives") -- by the Publishing House of the Academy of Sciences USSR in 1947. Five subsequent collections under the name "Physics of Explosion" were released in limited circulation in 1952--55; they contain many interesting investigations, carried out mainly by the Institute of Chemical Physics of the Academy of Sciences USSR and from 1959 are widely quoted in Soviet scientific literature on the theory of explosives.

This collection includes articles chiefly on three divisions of the theory of explosives -- sensitivity to mechanical influences, slow thermal disintegration, and ignition of explosives.

The first division starts with an article by the founder of comtemporary presentations about the mechanism of excitation of an explosion during shock, N. A. Kholevo, for the first time printed in "Physics of Explosion" in 1955. The second article is the report of the well-known English investigator F. F. Bouden, done by him in the D. I. Mendeleyev Moscow Chemical and Technological Institute in 1959. Many ingenious experiments by F. F. Bouden and his collaborators showed the large, sometimes decisive role, that can be played by gas bubbles during excitation of an explosion, especially in the case of liquid explosives. The work of K. K. Andreyev and Yu. A. Terebilina on the appearance of an explosion during shock on a drop-hammer are the continuation and development of presentations and investigations by N. A. Kholevo. The last (8th) article of the division is a survey of foreign works in this field. The authors of these works come to conclusions analogous to those, which for the first time were made by N. A. Kholevo.

A large part of the articles of the division refers to the investigation of thermal disintegration of nitroglycerine and in a lesser degree to disintegration of other nitro esters and partly nitrites. In spite of a certain onesidedness of the used (manometric) methodology in these works they succeeded to establish stages of decomposition of nitroglycerine and to uncover the physicochemical essence of the main stages, and also the influence on disintegration of different admixtures, in the first place, water and acids.

Three articles of the division (22, 23, and 24) are devoted to thermal disintegration of nitrocompounds, in particular, picric and styphnic acids and their salts. They established the complicated multistage character of decomposition of these compounds; the corresponding kinetic characteristics of disintegration and peculiarities of ignition of indicated acids and their salts are not observed. Proceeding from this, the authors arrive at the essential conclustion that the processes taking place in the condensed phase are not essential in the ignition of these substances.

The investigations, united in the third division, refer to several, but very essential sides of ignition. As in the work by B. N. Kondriko (Article 29) the paradoxical stabilizing influence of an admixture of lead azide and the increase of pressure on the ignition of liquid notro esters is shown. In the works by A. I. Gol'binder are described for the first time the pheonomenon of fractional burning-out during ignition of multicomponent volatile mixtures, established by this man and also the peculiarity of self-ignition of liquid mixtures, their burning, and the transition of the latter into an explosion. In the work by B. N. Kondrikov (Article 35) with the help of a new simple method the intensity of the flash of explosives, depending upon temperature, weight and other factors was quantitatively studied. Several interesting regularities are established, in particular, the decrease of intensity of flash of certain substances at an increase of temperature and absence of this phenomenon for initiating explosives. In the works by K. K. Andreyev and V. V. Gorbunov are considered the essential factors of acceleration of burning of crystal explosives -- cracking of their particles under the action of thermal shock and penetration of burning into the depth of a powder explosive; an attempt is made to provide a generalized diagram of the disturbance of stability of burning of powder explosives and to establish the main conditions leading to this disturbance.

The works by I. Ya. Petrovskiy and L. V. Volkov, K. K. Andreyev and V. G. Khotin are devoted to the technically urgent question of detonation and ignition of protective explosives.

Finally, in the articles in the fourth division, various phenomena connected with the appearance of detonation, and certain other questions are brought up.

The works considered in Articles 3, 7, 8--24, 26--29, 33, 35--37, and 40--42 were accomplished by the D. I. Mendeleyev Moscow Chemical-Technological Institute, the remainder -- by other research establishments.

All articles included in the collection were submitted to the publishing house before 1 March 1962.

Scientific editing of the collection was done by Professor K. K. Andreyev (Articles 19--21, 25, 32, 38, 39), A. F. Belyayev (Articles 26, 29--31, 34--36, 40--43), A. I. Gol'binder (Articles 1--8, 11, 17, 22-24, 27, 28, 33, 37), and A. G. Gorst (Articles 9, 10, 12--16, 18).

MT-63-254 Chapter 1 Article 1

Theory of Explosives, Moscow 1963

Pages Cover-9

I. SENSITIVITY OF EXPLOSIVES TO MECHANICAL INFLUENCES

N. A. Kholevo /Deceased/

1. Concerning the Question of Excitation of Explosion during Deformation of the Explosive Charge

As it is known, during deformation of a charge of a condensed explosive chemical transformation can appear, which, depending upon the speed of process, is called: burning, flash, explosion of detonation; in the future we will consider such a transformation under the general name "explosion".

Probability of the appearance of explosion at definite conditions of deformation of charge is a criterion of the sensitivity of the given explosive to mechanical influence, its ability to be exploded.

Deformation of an explosive charge may occur upon impact of a load falling on it, in the action of a shock wave and with a sharp change of the momentum of the charge, for example, in artillery missiles in the moment of firing and upon encounter with a barrier.

The author advanced general presentations about the mechanism of excitation of explosion by means of deformation of a small charge with drop-hammer impact. These presentations, after corresponding definitions, can be used also in other cases of action of external forces.

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[1] The article was prepared by the author for printing in 1954 and was published in 1955 in limited circulation. In subsequent papers, the author proposed to expound considerations about the mechanism of excitation of explosion and the relative sensitivity of an explosive at drop-hammer impact, and also about excitation of explosion in other conditions of deformation of an explosive charge.

In this article the role of stresses in excitation of explosion in case of deformation of an explosive is considered.

Role of Stresses in the Excitation of Explosion in a Deformed Explosive Charge

General Remarks on Deformation of a Charge with Drop-hammer Impact

The mechanism of the phenomena, occurring during deformation of a charge is very complex. Due to this, the author is limited to a qualitative interpretation of the essence of separate phenomena, although he does not negate the expediency of the attempts at quantitative calculations, undertaken, for example, in our time by Yu. B. Khariton [8].

A fundamental diagram of deformation of a charge at drop-hammer impact is presented in Fig. 1. Under the action of a falling load, possessing kinetic energy A, the upper striker, overcoming the resistance of the deformed charge, exerts pressure on the explosive. The first period of impact is characterized by an increase of specific pressure on the explosive to a certain maximum magnitude P, and the second period -- its decrease.

In Fig. 1 the state of a charge at the beginning and end of the first period of impact is shown. Work of deformation of the charge in this period is composed of work of pressure and work of flow of the explosive.

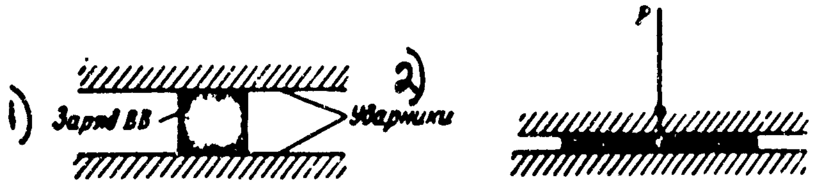

Fig. 1 Fundamental diagram of deformation of a charge at drop-hammer impact. 1) Explosive charge; 2) Strikers.

For a qualitative interpretation of this process equation (1) can be written in general form, corresponding to the end of the first period of impact.

$$A = A_o + W_m + \frac{p^2 V}{2K} + W \text{ explosive,} \qquad (1)$$

where A — energy of impact;

A_o — potential energy of elastic deformation of metal of the instrument and drop-hammer;

W_m — energy, "absorbed" by the metal of the instrument and drop-hammer as a result of plastic flow, external friction etc.;

$\frac{P^2V}{2K}$ — work of pressure of charge (V — volume of charge; P — stress in charge at impact; K — modulus of thorough explosive pressure);

$W_{explosive}$ — work of flow of charge.

In the second period of impact, the potential energy of elastic deformations $A_o + \frac{P^2V}{2K}$ is transformed mainly into energy of load rebound, which one can determine by the height of rebound.

Upon examination of equation (1) and Fig. 1 the following general remarks can be made.

1. Magnitude of stresses P in the charge is determined by its fluidity and external conditions of flow, and besides, the fluidity of the charge in a strong degree depends on the melting temperature of the explosive, while the external conditions of flow depend on the design of the instrument, in which the charge is deformed.

2. By measure of growth of stresses P, the speed of flow of the charge is decreased due to the increase of decelerations of movement of the upper striker.

3. Increase of work of pressure $\frac{P^2V}{2K}$ should be accompanied by a decrease of work of flow $W_{explosive}$ of the charge and vice versa.

In 1912 at the VIII International Congress on Applied Chemistry, for testing the sensitivity of an explosive at drop-hammer impact the so-called Kast instrument was adopted. This instrument, somewhat modified by the All-Union Government Standard 2065—43, in the future will be called "instrument No. 1".

For creation of conditions of deformation of a charge, accompanied by stresses smaller, than in instrument No. 1, the author in 1946 offered instrument No. 2. For excitation of stresses in a charge greater, than in the use of instrument No. 1 the author in 1950 developed instrument No. 3 (diagram of instruments No. 1, 2 and

3, see Fig. 2). In using a ring in instrument No. 3 for solid explosives and for liquid explosives a cup[1] made from different non-ferrous metals (lead, tin, aluminum, copper et al.), it is possible to excite larger or smaller stress in a charge independent of the fluidity of the explosive. To receive the desired stress during deformation of a charge in instrument No. 3 is also possible by changing dimension a on the upper striker (See Fig. 2).

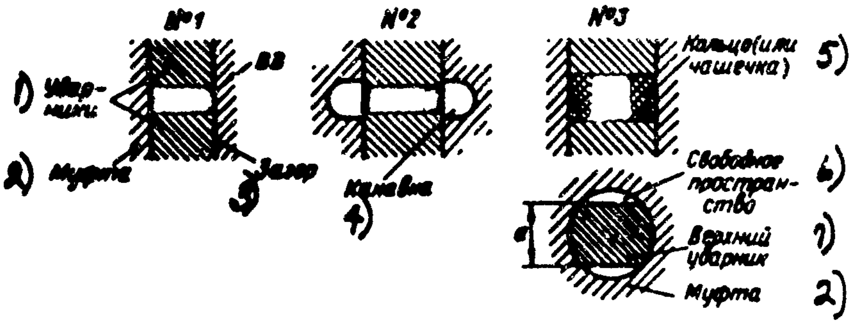

Fig. 2. Diagram of instruments for testing explosives with a drop-hammer. 1) Strikers; 2) Sleeve; 3) Gap; 4) Groove; 5) Ring (or cup); 6) Free space; 7) Upper striker.

Application of the instruments described above allowed for experiments to be conducted, when at constant impact energy in the charge very large or very small stresses were excited, when these stresses were determined mainly by the fluidity of the charge (instrument No. 2) and when the fluidity of the charge did not render a determining influence on the magnitude of stresses (instrument No. 3). Results of the experiments allowed to compare the stresses excited in the charge, and the probability of the appearance of explosion which provided a basis for criticism of wide-spread erroneous presentations on the role stresses in the deformation of an explosive charge.

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[1] In an instrument with a striker 10 mm in diameter, the ring has an external diameter of 10, internal 6 and height 3 mm. After introduction of 0.05 g of explosive and pressing the height of the ring becomes equal to approximately 2.3 and internal diameter of about 4 mm. The cup has an internal diameter of 4, height 3 and thickness of the bottom 0.3--0.5 mm.

Literary Information on the Role of Stresses

Kast [5], in analysing the data known to him(before 1920), made a conclusion that at impact, the probability of excitation of explosion is greater the more specific pressure on the explosive. Confirmation of such a conclusion he considered to be known from an experiment with the increase of sensitivity of an explosive in the presence of solid particles, on the outer limits of which in Kast's opinion, pressure is "concentrated".[1] The role of pressure Kast explained by excitation of high temperature. He allowed, however, for the possibility of direct excitation of explosion, passing the thermal stage.

L. Vennen, E. Burleau and A. Lecorche [3] allow that in certain cases, impact causes oscillation of molecules of a character, other than oscillations caused by the increase of temperature.

Brunswig [2] considers that besides a number of theoretical considerations against the assumption about intermediate transition of energy of impact into thermal energy, there is the absence of a parallelism between sensitivity to impact and temperature of flash which is difficult to explain even at calculation of distinctions in heat capacity, thermal capacity, coefficient of elasticity and so forth. This investigator allows that "to pressure, as the factor overcoming resistance, belongs, probably, the role of mutual approach of atoms with a large chemical affinity".

In 1922 Justrow [14] expressed the thought that the sensitivity of an explosive during firing and at drop-hammer impact is determined by critical stresses and that these stresses may be expressed by experimental means.

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[1] The presentation about the increase of sensitivity as a result of "concentration of pressure on the outer limits" is wide-spread and was entered in textbooks on the theory of explosives. Apparently, this last circumstance provoked the question frequently asked by the author at factories: "Is it safer to conduct mechanical processing of explosive charges with a sharp or a dull tool?"

The efforts of a number of investigators are known, the essence of the opinion of which on the role of stresses in the excitation of explosion is reduced to the above-indicated presentation [2], [4],[5], [14].

In connection with this it is necessary to note the interesting investigations of Yu. N. Ryabinina [6], [7], who studied the influence of static stresses up to 50 thousand kg/cm^2 on the thermal decomposition of an explosive. He established that these stresses not only do not increase the speed of decomposition, but for a number of explosives even delay it. Bridgman [11] studied the influence of static stresses up to 100 thousand kg/cm^2 on explosive. As a result of testing seventeen explosives, he arrived at the conclusion that under the action of such stresses an explosion is not stimulated.

The experiments of Ryabinin and Bridgman reject the affirmation of some investigators [12 et al.] on the possibility of excitation of explosion as a result of the direct action of static pressure. However, these experiments do not give an answer to the question about the influence of dynamic stresses, similar to those which appear in an explosive, for example, at drop-hammer impact, when the time of deformation of the charge constitutes 10^{-3} -- 10^{-4} sec.

An attempt to experimentally check the influence of dynamic stresses was undertaken by Tamman and Kroger [13]. However, the unsuccessful registration of experiments did not provide the possibility to the authors to make a definite conclusion.

On the basis of the brief account of literary information on the considered question the following conclusions can be made.

1. The presentations of Kast, Brunswig, Eggert, Justrow et al., advanced in 20 years, on stresses,as on the factor, determining explosive sensitivity, were developed in works, carried out during the period of the next 10—20 years.

2. The presentation about the determining role of stresses in excitation of explosion served as a basis for promoting the hypothesis of critical stresses which

also led to the selection of a definite direction for investigations of the stability of an explosive charge of an artillery shell upon firing.

3. The presentation about the determining role of stresses in excitation of explosion served as the theoretical basis of the opinion about the advantage of the method of exhibiting relative sensitivity of an explosive upon impact in instrument No. 1.

4. The wide-spread presentation about such a role of stresses in an explosive is accompanied according to a number of authors by the denial of an intermediate thermal stage and promoting of the hypotheses on triggering of an explosion as a result of "decrease" or "increase" of distances between molecules and atoms.

Experimental Check and Discussion of Information on the Role of Stresses Known in Literature

The author first [10] established that with a drop-hammer impact certain explosives possess less sensitivity in instrument No. 1, than in instrument No. 2, although in the latter there appear smaller stresses, than in the first. Establishment of the high sensitivity of the explosive in instrument No. 2 served as a basis for criticism of the wide-spread presentation on the role stresses in triggering an explosion.

In Table 1 are examples, illustrating the noted phenomenon. In a series of cases (experiments 1, 2, 6, 10) the frequency of explosions in instrument No. 1 is greater than in instrument No. 2. Also in the Table are cases, when the frequency of explosions in instrument No. 1 is significantly less than in instrument No. 2 (experiments 3, 5, 7, 8, 9, 11) which is not completely coordinated with the presentation on stresses, as the main factor determining sensitivity of explosives. In Table 1 are the results of experiments, when in the presence of paraffin, sensitivity of explosive in instrument No. 1 is greatly increased (compare experiments 5 and 6 or 9 and 10) which also is impossible to explain, being directed by the old presentation of the role of stresses in triggering an explosion.

Table 1

Sensitivity of explosive in instruments No. 1 and 2 (weight of load — 5 kg, weight of explosive charge — 0.05 g, number of parallel experiments — 20)

1) № опыта	2) Наименование ВВ	3) Энергия удара кГ·м	4) Частость взрывов % 5) прибор № 1	№ 2
	6) Тротил	4	20	0
	7) Тетрил	4	100	0
	8) Дымный порох	4	35	70
	9) Гексоген	2,5	80	90
	9) Гексоген+Al 10) (пудра) 50:50	4	0	—
	9) Гексоген+Al 10) (пудра) 50:50	2	—	100
	9) Гексоген+Al 10) (пудра)+ 11) парафин 45:45:10	2	40	0
	$KClO_3$+ 12) уголь 87:13	4	0	—
	$KClO_3$+ 12) уголь 87:13	2	—	100
	NH_4NO_3+Al 10) (пудра) 80:20	4	0	—
	NH_4NO_3+Al 10) (пудра) 80:20	2	—	100
	13) Пироксилин	2,5	30	100
	13) Пироксилин+ 11) парафин (95:5)	2,5	100	0
	14) Стифнат свинца	2	0	100

1) experiment; 2) Designation of explosive; 3) Energy of impact kG · m; 4) Frequency of explosions; 5) instrument; 6) Trotyl; 7) Tetryl; 8) Smoke powder; 9) Hexogene; 10) (powder); 11) paraffin; 12) carbon; 13) Pyroxyline; 14) Lead styphnate.

Thus, on the basis of the data in Table 1 a conclusion can be made that the probability of triggering an explosion is not always in direct dependence on the stresses appearing at impact and, consequently, the wide-spread presentations on the role of stresses in this process do not correspond to reality.

However such a conclusion is disputed by certain "protectors of stresses", who affirm that explosives possess "selective" sensitivity to impact and to friction[1]. This sensitivity to impact, in their opinion, is the most objective criterion of stability of explosives, stipulated by their chemical nature. In the opinion of these scientists, instrument No. 2 characterizes sensitivity only to friction,

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[1] By impact they imply deformation of a charge as a result of dynamic compression and by friction — as a result of flow.

and the results of testing in it do not depict therefore the influence of stresses and, in general, are not indicative. These considerations are scholastic and can easily be refuted by the results of experiments in instrument No. 1 given below.

The experiments in this instrument were conducted with a large number of explosive and nonexplosive substances. In the selection of substances for tests mainly their ability upon impact to be forced into the gap of the instrument was taken into account, which is stipulated by the yield point and melting point of the substance.

0.05 g of the substance was placed in instrument No. 1 and an impact was made, noting height of rebound of the load (only in cases of failure) and degree of pressing of the substance into the gap of the instrument. With every substance up to 50 tests were conducted and for comparable substances the external conditions of impact were observed with constants.

For the characteristics of the method of investigation and conclusions which were made in Fig. 3 and in Table 2, the results of the study of certain substances are given.

In Fig. 3 the vertical series of points correspond to the heights of recoil of load h_o at heights of its fall h, equal to 200, 400 and 600 mm. Every vertical series (with the exception of series V and VI, corresponding to aluminum powder and water) was obtained as a result of 20 parallel experiments.

Work of flow of the charge $W_{explosive}$ in the given case is connected with heights of fall h and rebound h_o of the load by an approximate relationship

$$W_{explosive} \approx 0.005\ (h - 1.70h_o)\ \text{kG} \cdot \text{m} \qquad (2)$$

In a separate series in Fig. 3 the points are absent, corresponding to cases of explosion. The number of such cases is marked by a digit in the circle, located above the corresponding series of points.

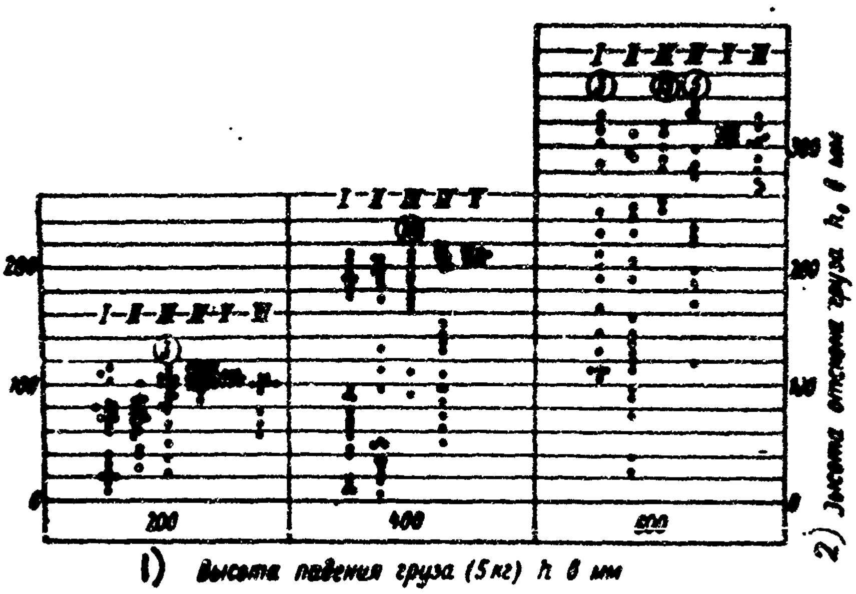

Fig. 3. Height of rebound of load in a series of parallel experiments with different substances on a drop-hammer: I — trotyl, II — dinitrobenzene, III — tetryl, IV — xylyl, V — aluminum powder, VI — water. (Figures in circle — number of explosions from 20 experiments). 1) Height of fall of load (5 kg) h in mm; 2) Height of rebound of load h_0 in mm.

Table 2

Relation of average height of rebound to height of fall of load (see Fig. 3)

1) Наименование вещества	Температура затвердевания 2) °C	3) Отношение $h_0:h$ в %		
		h мм		
		200	400	600
4) Тротил	80,7	38	19	33
5) Динитробензол	90	36	25	21
6) Тетрил	128,8	46	45	48
7) Ксилил	181	52	33	47
8) Алюминиевая пудра'	>600	52	51	51
9) Вода	0	50	—	50

1) Designation of substance; 2) Temperature of hardening °C; 3) Ratio of h_0: h in %; 4) Trotyl; 5) Dinitrobenzene; 6) Tetryl; 7) Xylyl; 8) Aluminum powder; 9) Water.

On the basis of the data in Fig. 3, Table 2 and certain observations the following conclusions can be made.

1. Upon impact the charge in instrument No. 1 is compressed and it flows. The work of the flow of the charge $W_{explosive}$ depends on the energy of impact and the fluidity of the explosive. In cases, when fluidity is very small (aluminum

powder) or when fluidity of the explosive and energy of impact is not great (xylyl at h = 200 mm), the work of flow of the charge, as follows from equation (2), is small, due to the fact that the charge is not forced into the gap of the instrument[1]. In those same cases, when plastic and viscous-plastic flow of the charge occurs in the gap of the instrument, the work of flow can reach a significant magnitude, sometimes exceeding half of the energy of impact.

Thus, the wide-spread presentation about the fact that in instrument No. 1 only compression of the charge takes place, does not correspond to reality, and the affirmation that the work of flow of a substance in this instrument is small, is the result of a poor study of the mechanism of deformation of the charge.

There is no basis also to the proposal of certain investigators to consider that the results of tests in instrument No. 1 characterize sensitivity to impact, and in instrument No. 2 — to friction.

Both instruments characterize sensitivity of an explosive during transient deformation of compression and flow of a charge; with this, in instrument No. 1 the speed of flow is less, and compression is greater than in instrument No. 2.

2. Observed in Fig. 3, the very great scattering of results in parallel tests is explained not only by the different magnitude of the gap in the applied instruments, but also by a series of accidental causes, affecting the degree of melting of the charge. In view of such great scattering, it is impossible to determine stresses in charges in cases of explosion on the basis of their measurement in cases of failure. Thus, for example, it is impossible to think that the stresses, leading to explosion of tetryl in 13 cases (h = 600 mm), are equal to the stresses in 7 cases of failure. The stresses in cases of failure can be very strongly distinguished from stresses in cases of explosion.

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[1] Work of flow is small also in those cases, when the charge possesses very large fludity (water).

3. In the vertical rows in Fig. 3 are points corresponding to cases of explosion. There arises a question: Which heights of rebound correspond to the discarded points? If these points corresponded to the greatest values of height of rebound, then the presentation about the determining role of stresses in triggering an explosion in certain degree would be experimentally confirmed. The answer to this question can be seen in Table 2, where the change of the ratio of height of rebound of load to height of its fall $h_o : h$ with the increase of height h is given. In cases of absence of explosions, the ratio $h_o : h$ with an increase of h from 200 to 400 mm is decreased (trotyl, dinitrobenzene, xylyl). If the cases of explosion corresponded to great heights of rebound, then the scattering of points would lead to a further decrease of the ratio $h_o : h$ with the increase of height of fall. In this case, at h = 600 mm the ratio $h_o : h$ for trotyl must have been less than 19, for xylyl - less than 33 and for tetryl - less than 45%. In reality, upon transition from a height of 400 to a height of 600 mm the ratio $h_o : h$ not only was not decreased, but was even noticeably increased. Such a result is due to the fact that explosions correspond chiefly to small values of height of rebound, i.e. explosions are triggered with smaller stresses, but in large work of flow - see equation (2).

Thus, the results of experiments in instrument No. 1, shown in Fig. 3, and also in Table 2 and 1 convince us of the fact that stresses are not the factor determining triggering of an explosion and that the wide-spread presentations about such a role of stresses do not correspond to reality.

The Actual Role of Stresses in Triggering an Explosion

During the study of the role of stresses in triggering an explosion, first of all it was necessary to explain their influence in the case when there is no flow of the charge. Such deformation of charge most successfully was obtained in instrument No. 3, in which plasticity of the metal of the ring ensured thorough pressure on the charge upon impact, and flow of metal in the gap of the instrument did not appear.

Experiments were conducted with trotyl, which was introduced in a quantity of 0.05 g to instrument No. 3 with a small gap and with an aluminum ring. After molding (or after preliminary impacts during fall of the load from a small height) tests were conducted during fall of a load weighing 5 kg from a height of 2000 mm. With this, there were no explosions.

In conducting a second series of the same experiments with an upper striker, having dimension a, equal to 9 mm (see Fig. 2), or with a lead ring instead of an aluminum one, 100% frequency of explosions was obtained.

In the first case, upon impact the ring was very insignificantly forced into the gap of the instrument (after impact this was checked by extracting the ring from the instrument) and, consequently, only thorough compression of the charge occurred, with the appearance of great stresses, but with a very small flow of it. In the second case, as a result of partial pressing of aluminum into the free space between the grooves of the striker and sleeve or lead into the gap of the instrument, a great flow of charge took place with smaller stresses[1] than in the first case.

Since in the first case the charge was subjected to thorough compression with very great stresses, then there appeared the assumption that in the deformation of compression of a charge not accompanied by flow of the explosive, an explosion is not triggered.

For checking this, precisely the same experiments were conducted, but with significantly more sensitive explosives than trotyl -- hexogene and PETN. The results of the experiments confirmed our assumption.

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[1] The magnitude of stresses is judged by the height of rebound of the load with the application of naphthalene instead of trotyl.

Specially interesting results were obtained with mercury fulminate, which, as it is known, is characterised by very high sensitivity. For conducting the experiments an instrument was used, a diagram of which is shown in Fig. 4. Into a copper ring with internal diameter of 5 and height of 2.5 mm 0.05 g of mercury fulminate was placed and with the help of a press, the strikers were pressed by force of 5000 kilograms. The instrument, after pressing, was subjected to consecutive drop-hammer impacts with fall of a load weighing 10 kg from heights of 150, 250, 500, 750 and 1000 mm[1]. With this, an explosion was not triggered off. After an impact from a height of 1000 mm, the instrument (without tray) was turned and the sleeve was moved downwards; as a result, the copper ring with mercury fulminate appeared against the groove of the sleeve and upon impact could be forced into the latter. The instrument prepared in this manner was subjected to impact at the fall of 10 kg load from a height of 150 mm. In these conditions, explosion of mercury fulminate was triggered. The phenomenon was constantly repeated in a significant number of independent tests.

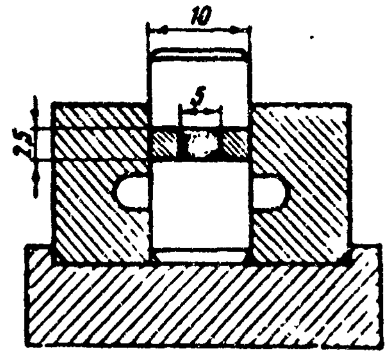

Fig. 4. Instrument for experiments with mercury fulminate.

In this manner, it was established that in case of thorough compression even of such a sensitive explosive as mercury fulminate, an explosion is not triggered, if flow of charge is very insignificant. Conversely, mercury fulminate with significant flow of charge explodes, although the stresses then are considerably less than in the first case.

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[1] A further increase of height of fall of load was not permitted because of apprehension of significant deformation of the sleeve of the instrument and the possible flow of the charge due to this.

The above-described experiments with trotyl, hexogene, PETN and lead fulminate convincingly confirmed the assumption that with thorough dynamic compression of a charge, not accompanied by its flow, an explosion is not triggered[1].

At the same time these experiments, just as the investigations described in the preceding division, confirm the thought expressed by author [9] that the effectiveness of mechanical influence should be considered, taking into consideration deformation of flow of the charge, and not deformation of its compression.

As an additional confirmation of this can serve the experimental data of S. M. Muratov, who in studying the relative sensitivity of several explosives in instrument No. 1, received the paradoxical results, given in Table 3.

The unexpected results of the experiments of S. M. Muratov are explained by the fact that he used instruments No. 1 with a very small gap between the striker and channel of the sleeve, due to which, impact was accompanied by very small flow of those explosives which possess poor fludity. As a result, in charges of such, very sensitive, but possessing low fluidity, of initiating explosives, as mercury fulminate, lead styphnate and lead aside, explosion appeared significantly more difficult, than in charges of PETN and trotyl, which possess good fluidity. However, from this it is impossible to make the conclusion that the named initiating explosive possesses less sensitivity during deformation, than PETN and trotyl. For revealing the relative sensitivity of explosives, possessing different fluidity, it is necessary to consider the conditions of flow of the substance of their charges.

Taking into consideration the results of the conducted experiments, a conclusion can be made that triggering of explosion of an explosive substance stipulated by the flow of the substance of the charge.

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[1] In the opinion of the author, this conclusion can be spread also in the case of triggering of larger stresses, than are accessible with drop-hammer impact. However this consideration does not have practical value, since very large stresses inevitably should be accompanied by flow of the charge, which also stipulates triggering of an explosion.

Table 3

Results of testing the relative sensitivity of explosives in instrument No. 1

1) Наименование ВВ	2) Энергия удара кГ·м	3) Частость взрывов %
4) Тротил	3	40
5) Тэн	3	100
6) Тетразен	3	60
7) Азид свинца	3	30
8) Гремучая ртуть	3	10
9) Стифнат свинца	4	10

1) Designation of explosive; 2) Energy of impact kG·m; 3) Frequence of explosions; 4) Trotyl; 5) PETN; 6) Tetrazene; 7) Lead azide; 8) Mercury fulminate; 9) Lead styphnate.

There arises, however, a question about the character of the influence of stresses in the charge, which inevitably accompany deformation of flow of the explosive.

In Table 1 are the results of experiments in which triggering of an explosion was stipulated by flow of the charge, accompanied by larger (experiments 1, 2, 6, 10) and smaller (experiments 3, 5, 7, 8, 9, 11) stresses.

With very large stresses and small flow of a trotyl charge in instrument No. 3 with an aluminum ring an explosion is not triggered, at smaller stresses, but larger flow of this charge in instrument No. 3 with a lead ring the frequency of triggering the explosion of trotyl is 100%. However at still smaller stresses, although with large flow of the charge in instrument No. 3 with a lead ring and upper striker having facets, explosion is not triggered.

Thus, the results of these experiments show the complex character of the dependence of the probability of triggering an explosion on stresses.

Considering that the appearance of an explosion is stipulated by the flow of the explosive, the determining parameter of this process can be considered as the specific speed of energy release u in the charge during its plastic flow. Magnitude u is greater, the larger the coefficient of internal friction η and gradient of speed of flow $\frac{dv}{dx}$. It is easy to show that

$$u=\eta\left(\frac{dv}{dx}\right)^2. \qquad (3)$$

It is possible to assume that the role of compression stresses is connected with their influence on the coefficient of internal friction, especially in cases of viscous flow.

Practical interest is presented by the dependence of speed of absorption of energy and speed of flow of explosives on stresses with constant energy of impact.

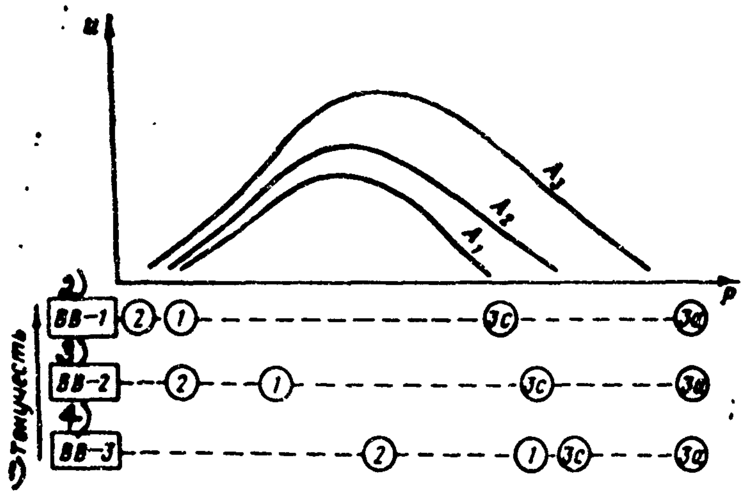

Fig. 5. Dependence of specific speed of energy release in charge (u) on the stresses appearing in it (P) with different impact energies (A) [Schematic graph]. 1) Fluidity; 2) - 4) Explosive - 1 - 3.

With constant energy of impact and increase of stresses, the speed of flow is decreased (see division 1). This circumstance stipulates the increase of u with the increase of P only up to a certain optimum magnitude. At a further increase of P, the speed of flow becomes so small that u starts to be decreased.

Consequently, at an energy of impact A = const, u = ψ (P), it is possible to present curves, having a maximum, as this is shown in Fig. 5. The curves in this figure express the dependence of u on P at energies of impact.

$$A_1<A_2<A_3.$$

Let us assume that in instruments No. 2, 1, 3c (lead ring) and 3a (aluminum ring) at energy of impact A_1 deformation of a charge of explosive - 1, possessing great fluidity is produced. The stresses, appearing in the deformation of this charge in different instruments, are shown in Fig. 5 by means of circles, in which the index of the corresponding instrument is written[1]. In the case of deformation of a charge of explosive -2, possessing lesser fluidity, than explosive -1, the corresponding circles are arranged somewhat more to the right[2]; but in case of deformation of a charge of explosive -3, possessing still lesser fluidity, the circles are arranged still somewhat more to the right.

Thus, P and u depend on the design of the instrument and fluidity of the explosive. The magnitude u in case of deformation of a charge of explosive -1 is very small in instruments No. 2 and 1 due to small stresses, and in instruments No. 3c and 3a -- due to very low speed of flow of the explosive. In case of deformation of a charge of explosive -2, the magnitude u is greatest in instrument No. 1, but in case of deformation of a charge of explosive -3, magnitude u is greatest in instrument No. 2.

With an increase of energy of impact (for example, to A_3), the circles marked in Fig. 5 also will be displaced to the right. Then the speed of energy release u is increased to a certain limit. However, displacement of circles to the right and increase of u depend on fluidity of the explosive and design of the instrument. Thus, for example, it is possible to consider that at an increase of energy of impact, displacement of circles to the right for explosive -1 is small and it is accompanied by an insignificant increase of u in instruments No. 2 and 1 and greater in instrument No. 3c.

Fig. 5 depicts only a general qualitative dependence of u on fluidity of the charge, design of the instrument and energy of impact. In reality, the influence

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[1] For determination of the magnitude of stresses it is necessary to drop a perpendicular to axis P from the center of the circle.

[2] With the exception of a circle corresponding to the stresses in instrument No. 3a. In the latter, the magnitude of stresses considerably does not depend on fluidity of the explosive.

of separate factors on magnitude u is significantly complex. In particular, maximum magnitude u considerably depends on the degree of nonuniformity of the physical properties of the charge and on accidental deviations (see Fig. 3).

With the help of Fig. 5 it is possible, however, to explain the role of stresses during flow of the charge and a number of phenomena, that take place in drop-hammer impact. Allowing that the frequency of explosion is a direct dependence on u, it is easy to explain the rests of drop-hammer impact tests (see Table 1 and 3), which is impossible to witness, being directed by conventional presentations about the mechanism of impact. For example, considering that fluidity of trotyl and tetryl (see Table 1) corresponds to the fluidity of explosive -2 (see Fig. 5), it is easy to explain the insensititity of these explosives in instrument No. 2. The assumption that the fluidity of lead styphnate, pyroxylin, mixture of hexogene and aluminum powder and other explosives (see Table 1 and 3) corresponds to the fluidity of explosive -3, explains the lower sensitivity of these explosives in instrument No. 1 as compared to the sensitivity in instrument No. 2.

Thus, the various sensitivity of explosives in instruments No. 1 and 2 is explained by the different speed of energy release in the deformation of charges in these instruments, and not the scholastic "selective sensitivity of explosives to impact and to friction", as this is presented by certain investigators.

General Conclusions

1. By experimental means it was established that in cases of low speed of flow of a charge, an explosion is not triggered even with very large stresses. On the basis of this it is possible to consider that triggering an explosion is conditioned by the flow of the charge.

2. The effectiveness of the action of mechanical forces during flow of the charge is determined by the specific speed of separation of mechanical energy, which depends on the coefficient of internal (and external) friction and the gradient of speed of flow.

3. With a constant energy of impact, the maximum speed of energy release takes place at a certain optimum magnitude of stresses, which is possible to attain by means of application of a corresponding design of the instrument.

4. The wide-spread presentations on the critical stresses of explosives contradict experience and, consequently, are erroneous. Based on these erroneous presentations, the investigations of stability of a charge upon firing appeared therefore barren.

5. The concept of "selective" sensitivity of explosives "to impact" and "to friction" is erroneous, since triggering of an explosion is determined by the flow of the charge, which is characterised by the friction coefficient and the gradient of speed of flow.

6. Erroneous also is the concept of the fact that instrument No. 1 characterises sensitivity "to impact", but instrument No. 2 — "to friction". Every possible means of mechanical influence (independent of the design of the instrument) can characterise sensitivity only at flow of the charge. However, the coefficient of friction and gradient of speed of flow can strongly change, depending upon the means of mechanical influence.

7. The presentation about the fact that relative sensitivity in instrument No. 1 is the most reliable criterion of relative "stability" and safety of the charge is erroneous and obstructs the development of means of studying the sensitivity of explosives.

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Tape No. MT 63-254 Chapter 1 Article 2

Pages 20 - 36

F. Bouden

2. Recent Investigations of Decomposition of Hard Type Explosives (VV[1])

Explosion of hard VV can be caused by:

Heating to temperature of ignition;

Light of sufficient intensity;

Impact or shock;

Ultrasonic oscillations;

Action of electrons, α -particles, neutrons and fragments of nuclear fission;

Electric discharge;

"Spontaneous" /instantaneous/ decomposition as of growing crystal.

In this report questions are considered, referring to triggering of an explosion of hard VV by the three first forms of influence.

Triggering of Explosion by Heating

The investigators of the laboratory of Cambridge University follow, as well as scientist of the USSR, the view that an explosion most frequently appears from a heat-up of explosive. The condition of its appearance is a heat liberation with speed, exceeding its elimination speed. The theory of this complicated phenomenon was developed in the USSR by D. A. Frank-Kamenetskiy. According to investigations, conducted at Cambridge University, during a heat-up of several microseconds, the dimension of the heated region is within the limits 10^{-3} — 10^{-5} cm.

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[1] This article is an account of a report, read by Prof. F. Bouden of Cambridge University to the Mendeleyev Moscow Chemico-Technological Institute in March 1959. The article is prepared for publication by B. N. Kondrikovyi.

It is possible to show in a simple example that for the appearance of an explosion it is necessary that the characteristic dimension of crystal be not lower than a certain critical magnitude. If we place crystals of azide of cadmium in a thermostat, having a temperature of 320°, then only crystals with a thickness of 10^{-3} cm are exploded, crystals thinner than 10-5 cm are decomposed without explosion. Critical thickness of crystal depends on temperature, as this also follows from the Frank-Kamenetskiy theory.

Thermal decomposition of crystals of VV was also studied, occurring lower than a temperature of self-ignition. For this purpose an electron microscope was applied with a high resolving power, which attained 5Å, under laboratory conditions. This is almost an atomic dimension. Prof. Menter attempted to detect with the help of an electron microscope the molecules in crystal. He investigated under the microscope a crystal of phthalocyanin of platinum and received the picture, presented in Fig. 1. The streaks are rows of molecules, from which the crystal is built, the distance between them 12Å. It is clear that in one region the crystal is complete.

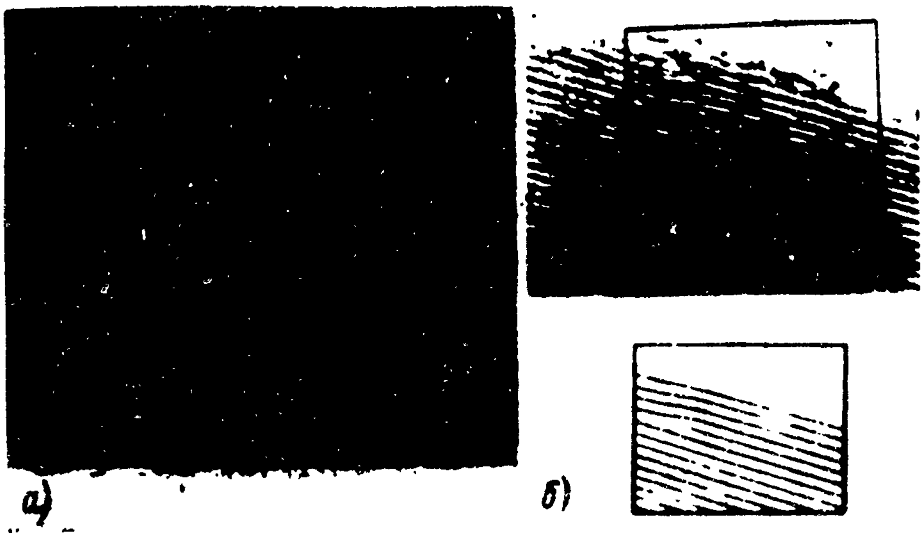

Fig. 1. Electron photomicrography of crystal phthalocyanin of platinum. Magnified approximately 1 million times; rows of molecules are noticeable in crystal; distance between atomic planes 11. 9Å). a) A section of crystal surface without defects. b) A section of surface with dislocation.

In other regions, however, it is possible to detect much different dislocations. We consider that chemical transformation appears preferably on dislocations.

Crystal of azide of silver under investigation in electron microscope (Fig. 2 and 3) is decomposed as a result of heat-up by its electron flow. On the surface of the crystal, on which the decomposition chiefly occurs lumps of silver will evolve. In Fig. 2 the nuclei are noticeably weak. In Fig. 3a dimension of nuclei changed insignificantly, but the contrast is very noticeable. On the enlarged photograph (Fig. 36) the nuclei and silver, lattice are noticeable.

Fig. 4 depicts the Laue diffraction pattern of crystal of azide of silver, decomposed under action of electron flow of an electron diffractional chamber. In Fig. 4a is shown the electrongram of crystal of azide at the beginning of the experiment. Already at this stage it is possible to see that the azide began to be decomposed. In Fig. 4b relative intensities of spots changed somewhat. The change of intensity is even more clearly noticeable in Fig. 4c. Certain spots here are very bright, but their position as yet does not change. Intensity of rings, characteristic for electrongrams of metallic silver, increases.

One should note that the distance between atoms of silver in azide is approximately twice as great as in silver itself, for which reason according to the degree of decomposition of azide, the atoms of silver converge. After removal of all nitrogen (Fig. 4e) they occupy the normal positions peculiar to metallic silver.

The electron microscope together with electron--diffraction examinations in our opinion is a very important tool for the study of crystal decomposition.

Fig. 2. Electron photomicrography of crystal of azide of silver at the beginning of decomposition, at the moment, corresponding to Fig. 4a.

The electron beam here simultaneously results in decomposition of crystal by strongly heating it and allows us to track the progress of this decomposition (see Fig. 5). In a number of cases such a combination can prove to be inconvenient. Therefore for the investigation of crystal decomposition , we also used a grating electron microscope, in which an electron beam, reflected from the surface of crystal, runs around it, similarly as this occurs in kinescopes. In this case the capacity of the beam is insufficient to heat to crystal and cause decomposition. This construction was developed in Cambridge by Smith and Whetley. Fig. 6 depicts a needle of azide of silver with a thickness of nearly 1 micron on a heated silver plate. Decomposition begins in the defects of the crystal lattice from the end of the needle, that has good contact with the plate. As a result the crystal is crushed into small fragments, the dimension of which does not exceed 0.3 micron. Finally the whole crystal is turned into a multitude of angular lumps or small knots of silver (Fig. 7).

Cracking and splitting of crystals on heating is observed also in the case of other VV. Fig. 8 depicts a crystal of azide of cadmium before (a) and after heating at 317° (b). It is clear that on heating the crystal is cracked and is broken along crystallographic planes.

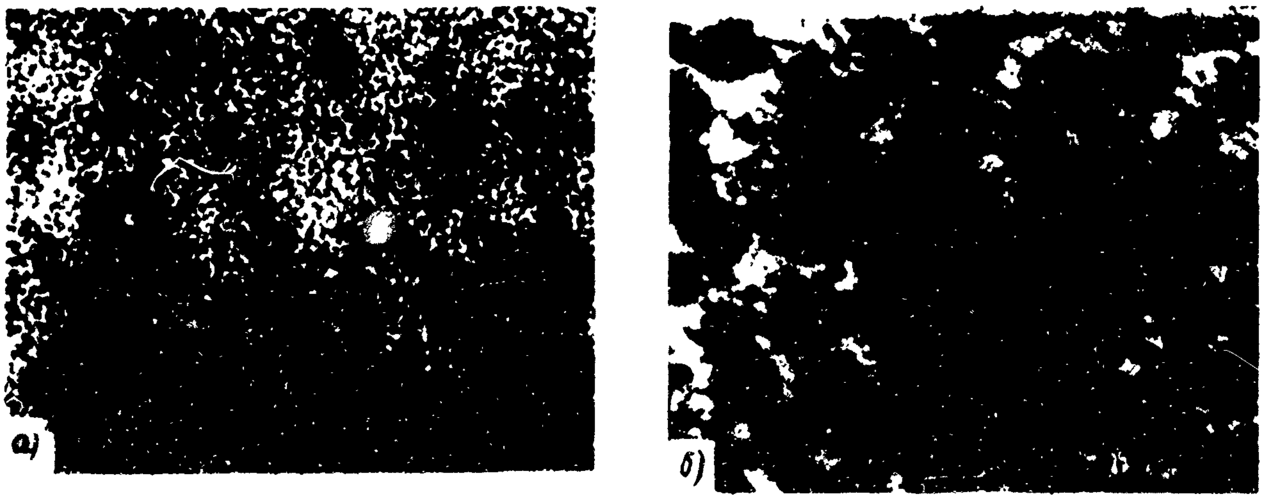

Fig. 3. Electron photomicrography of crystal of azide of silver, represented in Fig. 2 at the moment, corresponding to Fig. 4d.

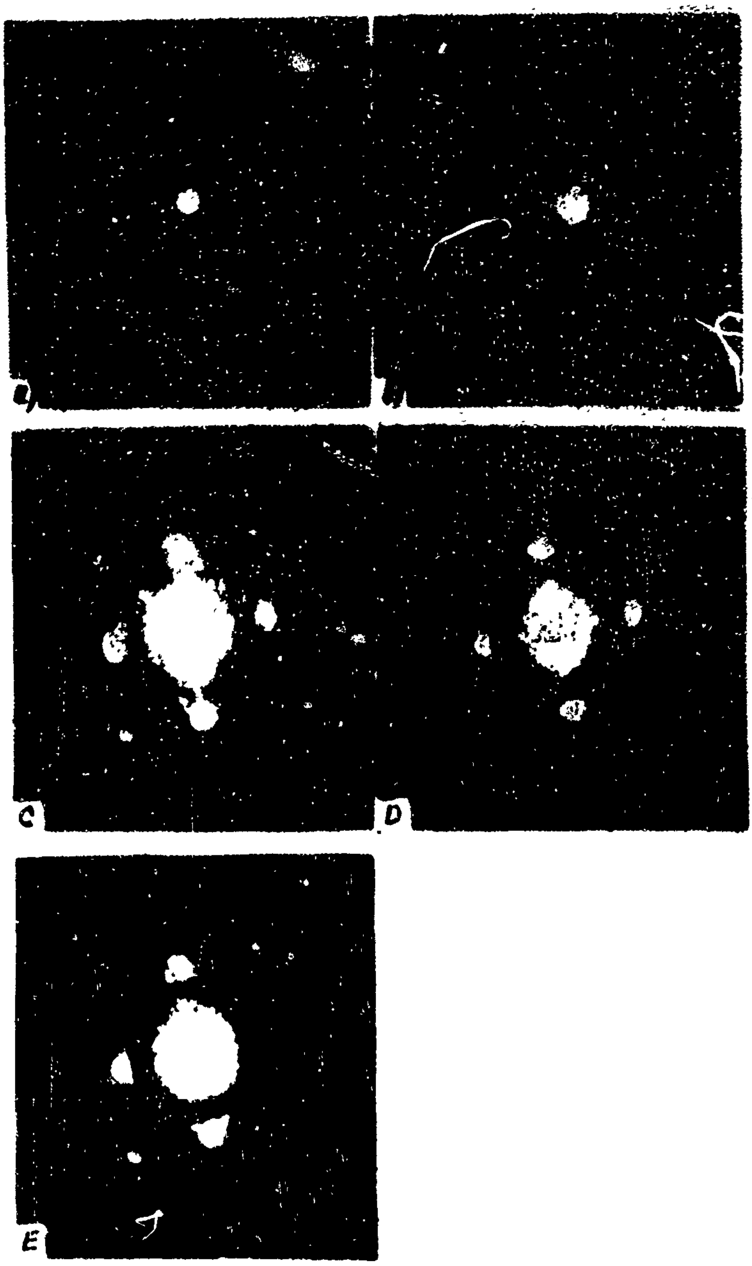

Fig. 4. Decomposition of azide of silver by electron flow. (Electrongram of crystal of azide of silver at different stages of decomposition).

In our opinion, which agrees with the ideas expressed recently by Prof. K. K. Andreyevi, the splitting of crystal on heating has a great value for the development of explosion in it. Fig. 9a depicts a crystal of TEN, subjected to the action of a powerful source of light and in Fig. 9b the same crystal before illumination. Explosion under this action does not occur, but the whole crystal is covered with a multitude of cracks. Therefore we conclude that decompositon of crystals of VV starts from the surface in dislocations and defects of the crystal lattice and leads to the splitting of the crystal into tiny fragments.

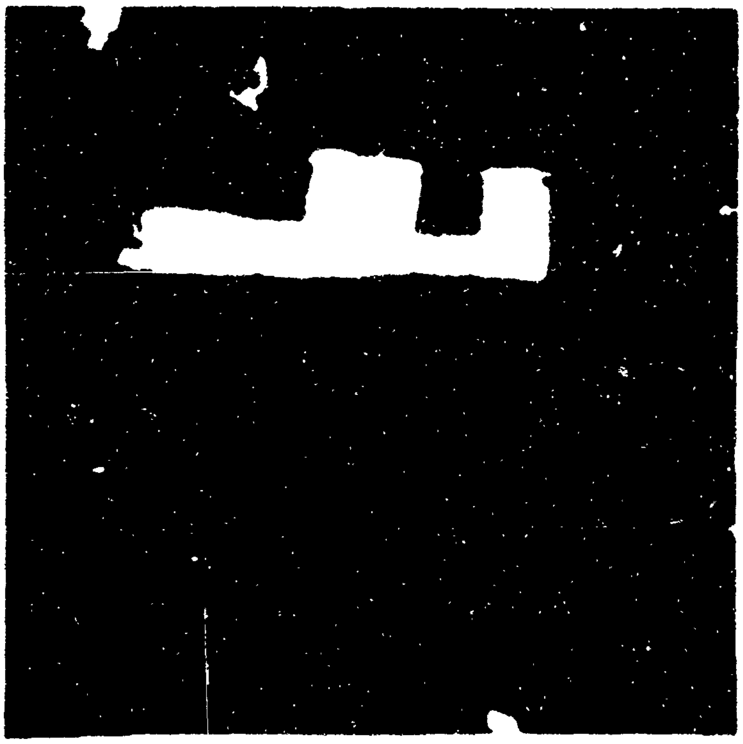

Fig. 5. Electron photomicrography of crystal of nitrate of potassium, fused under the action of electron beam.

Fig. 6. Partially decomposed needle of azide of silver.

Fig. 7. A needle of azide of silver, destroyed as a result of decomposition and crystallographic phase transition at 180°.

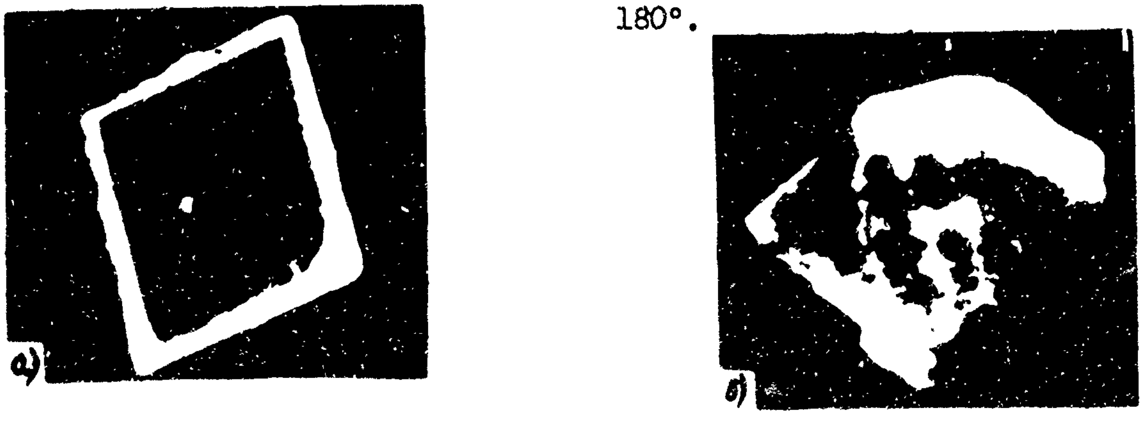

Fig. 8. A crystal of azide of cadmium before (a) and after (b) heating at 317° (magnified 440 times).

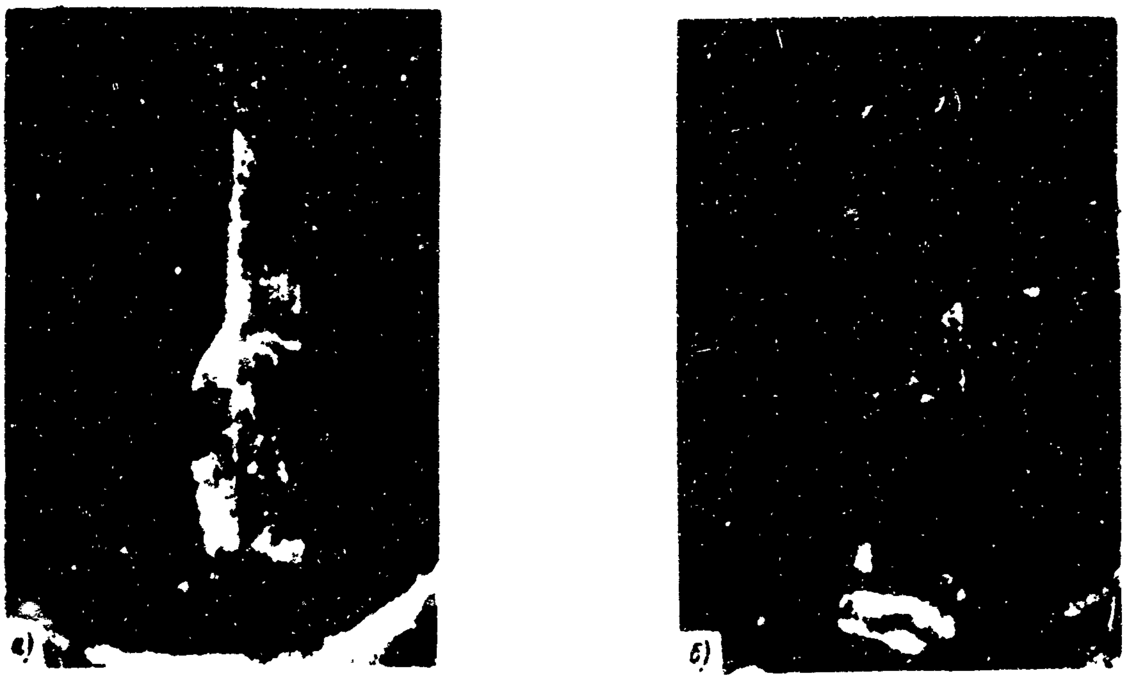

Fig. 9. Decomposition and cracking of a single crystal of TEN subjected to a pulse of light (energy 900 joule, duration 1.2 millisecond). a) Crystal after action of light pulse, b) Initial form of crystal.

Triggering Explosion by Light

A whole series of works, conducted in Switzerland and Cambridge, shows that crystals of VV can be decomposed under the action of light. If the intensity of the light source is sufficiently great, then some of the especially sensitive compounds are exploded. Secondary crystals of VV, basically covalent organic compounds, are not exploded even at energy of 2000 joule.

This form of triggering of explosive transformation is of interest in particular because during a short period of illumination (in our experiment it was about 1 millisecond) light is absorbed by a thin superficial layer, in which decomposition begins; deeper layers are not involved by the action of light, as a result of which we can avoid many complications, accompanying the triggering of an explosion by heat or impact.

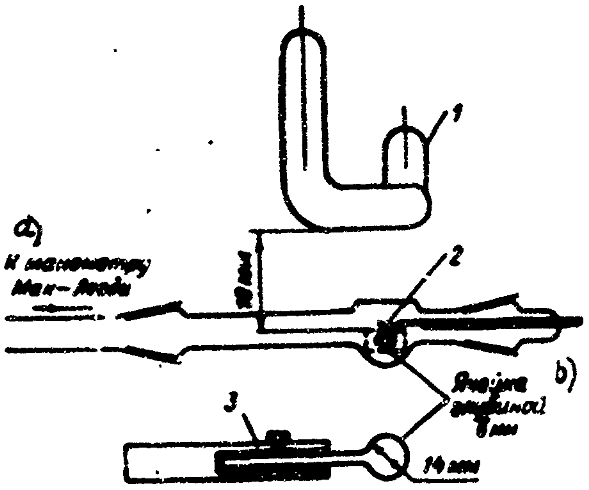

Fig. 10. Diagram of installation for investigation of triggering explosion by light. 1) Pulse tube, 2) Spoon with VV, 3) Holder. On diagram dimensions of the cell of the actinometer and its location (dotted line), are shown. a) To McLeod manometer, b) Cell with depth of 6 mm.

Certain results of works based on the action of light on crystals of VV can be used when examining the questions, connected with propagation of explosion and detonational phenomena.

Only a few substances are studied more or less in detail. They include azide of silver, azide of thallium, silver nitride, nitrogen iodide and lead styphnate. In the most detail was investigated azide of silver.

A diagram of the installation for investigation of the triggering of an explosion by light is presented in Fig. 10. The experiment shows that to trigger an explosion a certain critical quantity of radiant energy is required. Apparently, the process of triggering is photochemical: an ion of azide under the action of light is turned into a radical of N_3. If two radicals meet, then strong exothermal reaction occurs:

$$2N_3 \rightarrow 3N_2 + 210 \text{ kilocalorie}$$

So that this reaction may occur, in the first place, it is necessary to obtain two azide radicals and, secondly, they must meet.

If into VV we mix particles of metal, then these particles can act as traps of electrons and will remove electrons from an ion of N_3^-, transforming it into a radical. The effect of these particles on the magnitude of the critical energy of a light pulse is illustrated in Fig. 11.

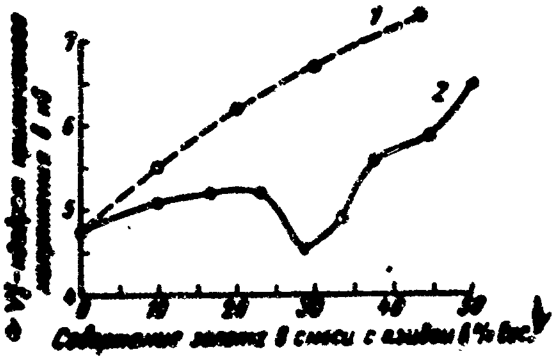

Fig. 11. Increase of sensitivity of aside of silver to light with the addition of gold particles. 1) Sensitivity of aside with inert diluent (calculation), 2) Its sensitivity based on results of experiments with addition of gold, V_c is the critical voltage on facing of capacitor in kv. (Light pulse is the spark in the air from two united parallel capacitors with a capacity of 8 microfarad each). a) V_c^2 is the square of critical voltage in kv; b) Contents of gold in mixture with aside in % of weight.

Indeed, the addition of gold lowers critical energy, instead of increasing it owing to the dilution of the substance, as can be seen from comparison of curves 1 and 2 Fig. 11.

We will note also that explosion of asides under action of light is frequently accompanied by melting of the surface layer; naturally the transformation of an ion into a radical and the exothermal interaction of two radicals occurs much faster and easier in the liquid than in the solid phase.

In the case of covalent azides and metalorganic compounds, for example, lead styphmate, the primary process, apparently, is not a photochemical reaction. Radiant energy in the final analysis transforms to thermal, and the explosion is developed by normal thermal mechanism. The decomposition of such compounds frequently occurs from the radical mechanism.

If we consider a series of ionic inorganic azides — KN_3, TlN_3, AgN_3, CuN_3, we will discover that the stability in relation to the action of heat and light decreases from the first to the last. KN_3 is a relatively stable solid substance, while AgN_3 is easily decomposed and under certain conditions explodes and detonates. The difference of ionization potential of metal and affinity to the electron of the aside radical in this series increases. It was shown that certain physical proper-

change in a parallel manner./
ties/ Change of structure, absorption spectrum, photoelectric conductance, refraction index, and melting point indicate that during an increase of the ionization potential of metal a deflection from an ionic type of lattice occurs. It is possible to show also that the energy, necessary to excite an electron and to transfer it from a strip of the valence to a strip of conductance, decreases; this determines the decomposition rate of azides of heavy metals (TIN_3, AgN_3 and CuN_3) and partially explains their instability.

Triggering of Explosion by Impact. As a rule triggering of explosion by impact is based on the process of heat-up of a substance. This heat-up can appear in different ways:

Adiabatic compression of gas pockets;

Heat-up during friction between surfaces, limiting the charge, or between the hard particles in it;

Friction between small crystals of the VV itself;

Viscosity heat-up of VV at high speeds of movement;

Heating of a sharp shock during plastic deformation;

Interaction of weak shock waves.

We will consider only some of these ways.

The most dangerous factor with respect to triggering of explosion on impact is the presence in liquids and also in certain solid VVs of a small quantity of air in the form of small bubbles. If, in order to trigger an explosion of nitroglycerine, freed from air bubbles, energy is necessary of the order of 10^5—10^6 g-cm, than with small bubbles 0.1 mm in diameter an impact with the energy of 20-100 g-cm is sufficient to trigger an explosion.

The air, in the bubbles, can be replaced by any other gas under the energy of the impact, necessary to trigger the explosion. It will be changed apparently, to the extent of the change of ratio of the heat capacities of this gas at constant pressure and constant volume C_p/C_v.

The presence in a liquid explosive of air bubbles promotes triggering of explosion by shock wave. Interesting experiments were conducted recently by Winning. He explodel a charge of nitroglycerine (see Fig. 12) alongside pipe, containing nitroglycerin (see Fig. 12) with air bubbles introduced into it; apparently explosion in the pipe occurs precisely where the bubble is.

During friction of two surfaces with VV between them the seats of heat-up, also are causes of ignition. Fig. 13 presents an oscillogram obtained when triggering an explosion by friction. Explosion appears at that moment, when the curve abruptly descents. (In Fig. 13 this moment is marked by vertical line A).

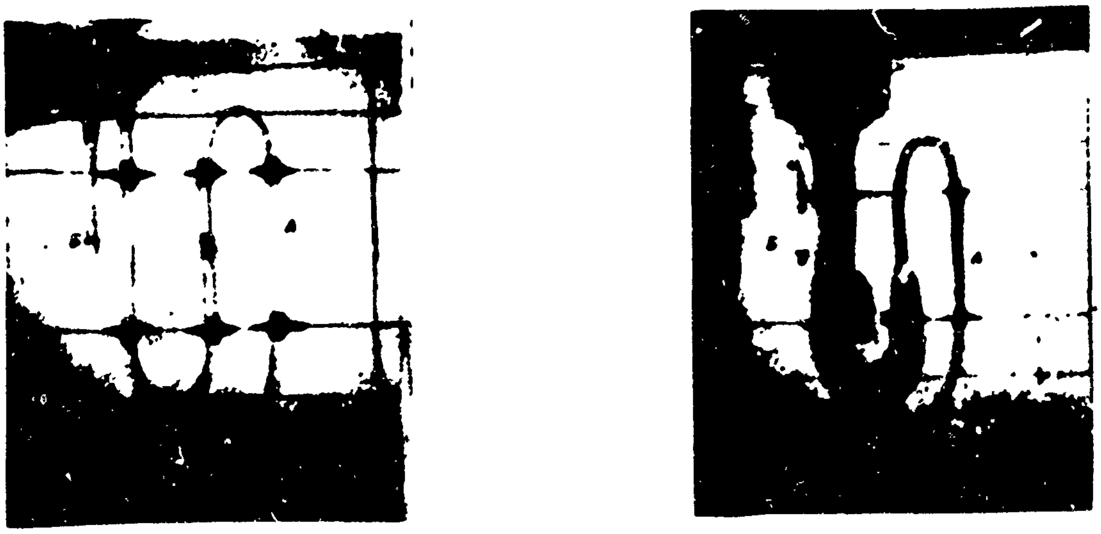

Fig. 12. Triggering an explosion of nitroglycerine by shock wave in water (after Winning). a) Pipe with nitroglycerine, b) Passive charge of nitroglycerine with small air bubble in lower part, (a) and (b) - system before explosion and at moment of its explosion.

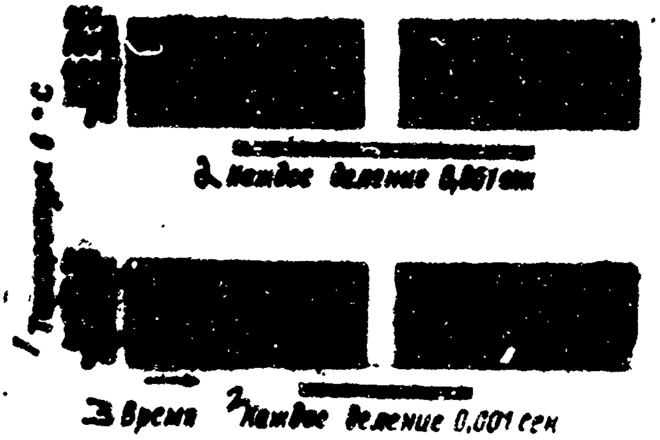

Fig. 13. Recording by cathode oscillograph of thermoelectromotive force with a slider of constantan moving along a steel surface, covered with a layer of nitro glycerine. On the left is the scale of temperatures in °C. 1) Temperature in ° 2) Each division 0.001 sec.; 3) Time. If temperature does not reach 400°, then an explosion is not observed.

Interesting also is the experiment concerning the triggering of an explosio by friction in the presence of hard particles. We detected that the important property of such a particle is its melting temperature. If it is lower than 50C then the explosion does not occur.

Table

Triggered Explosion of TEN by Friction in the Presence of Inpurities

(See Table On Following Page)

Table

	Примесь 1	Твердость по шкале Мооса 2	$t_{пл}$ °C 3	Частость взрывов % 4
5	Без примесей	1,8	141	0
6	Азотнокислый аммоний	2—3	169	0
7	Бисульфат калия	3	210	0
8	Азотнокислое серебро	2—3	212	0
9	Двухромовокислый натрий	2—3	320	0
10	Уксуснокислый натрий	1—5	324	0
11	Азотнокислый калий	2—3	334	0
12	Двухромовокислый калий	2—3	398	0
13	Бромистое серебро	2—3	434	50
14	Хлористый свинец	2—3	501	60
15	Иодистое серебро	2—3	550	100
16	Бура	3—4	560	100
17	Висмутит	2—2,5	685	100
18	Стекло	7	800	100
19	Каменная соль	2—2,5	804	50
20	Медный блеск	3—3,5	1100	100
21	Свинцовый блеск	2,5—2,7	1114	100
22	Кальцит	3	1339	100

1) Impurity; 2) Hardness by Mohs scale; 3) Melting temperature °C; 4) Frequency of explosions %; 5) Without impurities; 6) Ammonium nitrate; 7) Sulfate of potassium; 8) Silver nitrate; 9) Bichromate of sodium; 10) Sodium acetate; 11) Potassium nitrate; 12) Bichromate; 13) Silver bromide; 14) Lead chloride; 15) Silver iodide; 16) Borax; 17) Bismuthite; 18) Glass; 19) Rock salt; 20) Copper glance; 21) Lead glance; 22) Calcite

From the above table it is clear that substances, possessing different hardnesses, but with near melting temperatures render in this experiment approximately identical action.

An explosion of cyanurtriazide can be triggered by a blow with a metallic needle on the anvil, on which it is located. The sharp end of the needle during this is deformed and heated, while the explosion occurs at a temperature of about 300°--350°. Fig. 14 presents oscillograms, obtained in the experiment, in which a striker with a needle of tungsten smashes on a steel anvil.

At an impact energy of 1100 g-cm (Fig. 14a) the maximum rise of temperature (250°) is insufficient to cause an explosion of cyanurtriazide with an initial temperature of 95°. With the achievement of a temperature of 300°--350° impact energy of 3300 g-cm--Fig. 14b) explosions of this substance occur with 100% frequency.

In conclusion let us consider the question of the mutual strengthening of weak shock waves. Fig. 15 presents photographs, obtained in the winning experiments on triggering an explosion of nitroglycerine by shock wave. It is quite clear that two or three shock waves from active charges jointly trigger an explosion of a passive charge, at the time when one wave cannot trigger it.

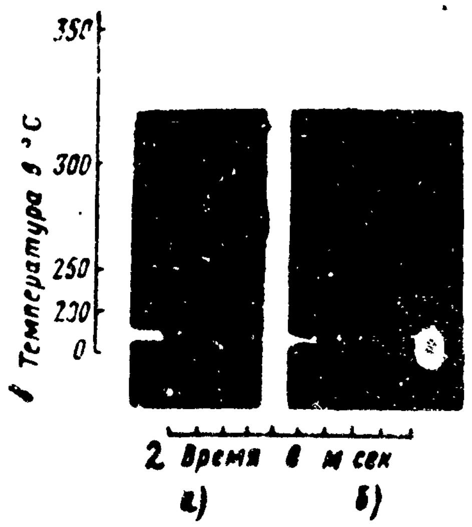

Fig. 14. Recording by cathode oscillograph of temperature rise on impact during flow of tungsten needle on a steel anvil. a—heat-up to 250°, no explosion; b—heat-up to 300°—350°, frequency of explosions 100 %. 1) Temperature in °C; 2) Time in m sec.

At present at Cambridge University work is being conducted on the study of explosion in separate crystal. Those precise methods, which were related at the beginning of this report, can be applied during the study, not only of slow, but also of instantaneous processes. This is a very interesting area of the investigation, since in one and the same crystal it is possible to observe slow decomposition and transformation, spreading with a speed of 7 km./sec. It is very interesting to establish what kind of connection exists between slow decomposition and rapid processes. The further improvement of apparatus and methods of investigation could introduce a real contribution in the development of this interesting area in the science of explosives.

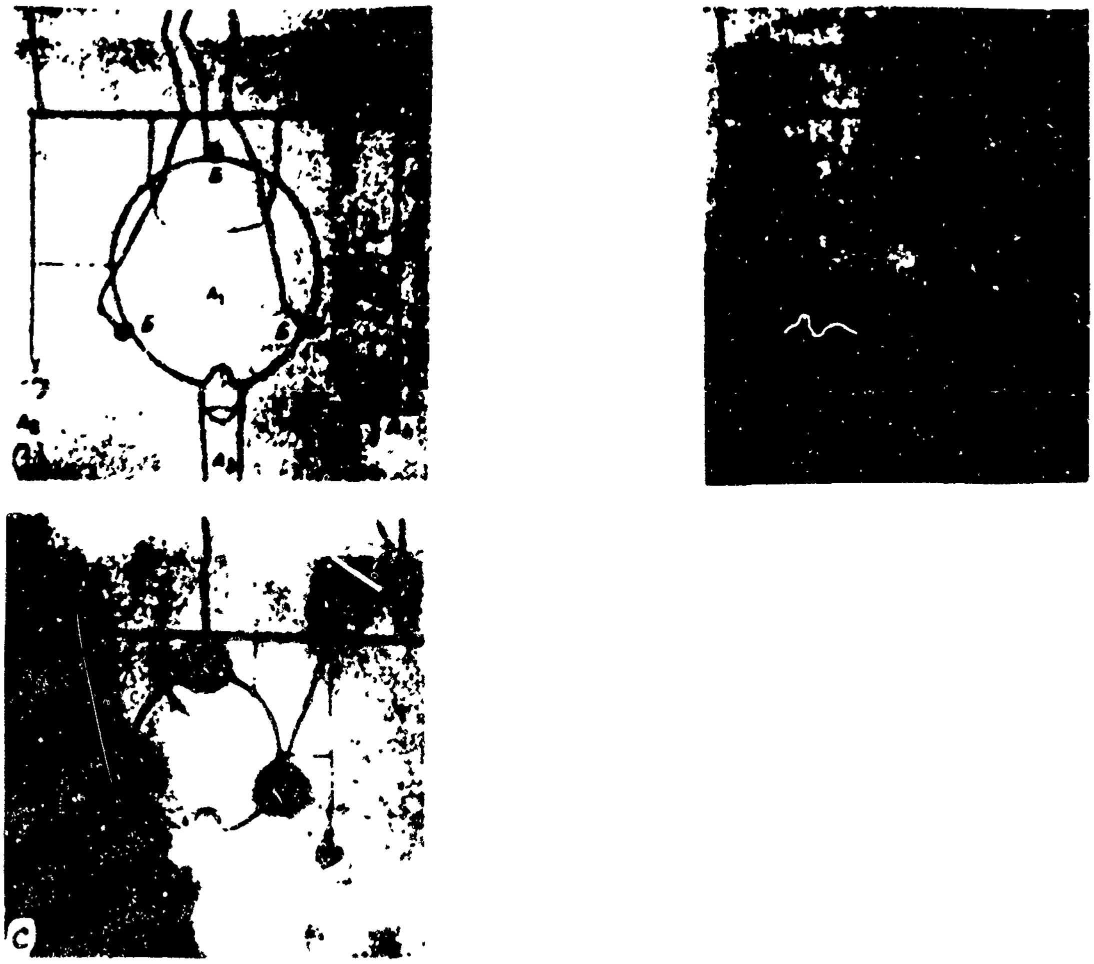

Fig. 15. Generation of explosion during the addition of shock waves, propogated in water (after Winning). A_1, A_2, A_3, A_4—passive charges of nitroglycerine, B—active charges. a) system before explosion, b) system in moment of explosion, c) system in moment of explosion at decreased distances between active and passive charges.

Discourse On The Report of F. Bouden

E. G. Ledin

The works of Prof. Bouden are recent; they are directed toward studying the mechanism of generating an explosion, and from this point of view his report, as a book, translated into Russian, is of positive interest. Prof. Bouden related to us delicate experimental investigations with the application of very interesting methods, allowing the study of explosion in its most initial stage. Those investigations, related by Prof. Bouden and the published monographs, are a new contribution to the theory of generating an explosion, and we must congratulate Prof. Bouden, for presenting this new work.

With a positive impression from the book and report it is impossible not to note certain peculiarities, that seem to me very essential. Prof. Bouden defends the assumptions of thermal triggering of explosion. The essence of this assumption consists in the fact that the triggering of an explosion occurs only after the explosive obtains sufficient temperature. The assumption based on thermal theory, assumes the transition from mechanical effect on VV to chemical reaction through heat-up, which according to this theory should precede the process of decomposition. This basic assumption is, in my opinion, the weak spot in the theory. Indirect ways in nature are not certain. Between the generation of an explosion and its continuation there should not be a break, otherwise it is difficult to correctly explain the process of decomposition; on the other hand it is difficult to imagine the universality of a temperature of 500°, which is the condition of the explosion, and not its result. It appears as if a VV waits, until it heats to 500°.

Under the conditions of pressure, interaction between charge and environment occurs. It is expressed in the fact that all the system is brought to a state of strain. It is simply proven that this state of strain results in a change not only of the intracrystalline state, but also of the intramolecular. An internal dependence exists, that expresses this connection. We will take the most simple example:

it is known that if there is the simple bond $\underset{\diagup}{\overset{\diagdown}{-}}C-C\underset{\diagdown}{\overset{\diagup}{-}}$, then interatomic distance $r \approx 1.7\text{Å}$; if however there is double bond $>C=C<$, then $r \approx 1.4\text{Å}$; with the triple bond $-C \equiv C-$ we have $r \approx 1.2\text{Å}$. When atoms of carbon approach each other, then internal bonds appear between them and external bonds are lost. We should say that energy, expended on a change of distance is not an activation energy — this is binding energy, which should be considered separately and which, as the final result, leads to decomposition. The temperature of the system will have value; it determines its sensitivity, but during the mechanical effect of the system it will change due in the first place, to a change of intensity and stability of the chemical bond. It is impossible that the system, being loaded, would not change chemically, therefore its temperature cannot play a determining role in the generation of the explosion. The constancy of critical temperature (500°) for a majority of substances attests to the fact that this temperature is either connected with methodology, because it is neither individual, nor with the process of propagation, but by no means with the generation of the explosion.

Based on thermal theory the breakdown of the generation of an explosion is as follows: influence--temperature--decomposition (I--T--D); another more probable mechanism of this process is: influence--decomposition--temperature (I--D--T). Temperature is the result, but not the cause of the generation of explosive transformation.

K. K. Andreev

It is known that under an impact on an explosive it can be detonated. The question, how mechanical effect causes chemical reaction leading to explosion, is of great interest. Investigations of Bridgeman, Riabinin, Bouden and other investigators have shown that even very high pressures during static application do not cause explosion and an essential acceleration of chemical transformation. It follows from this that those stresses, which during the pressure of an impact are created in the explosive, by themselves do not cause the explosion. It was natural therefore, to assume that in dynamic conditions of the effect it can lead to heat-ups of VV, from which is developed the explosion.

In what ways can heat-ups generate in the explosive on impact? Bouden and his collaborators by numerous ingeneous experiments have shown that, at least in the case of liquids, the presence in VV of gas bubbles can lead to a great increase in their sensitivity on impact; explosions generate with incomparably less impact than they do in the absence of bubbles.

Investigators give a natural explanation for this observation based on the fact that bubbles of air, on impact, are quickly compressed, are highly heated up and ignite the explosive. The question how this igniting is accomplished is impossible, however, to consider explained. Apparently, here the essential role is played by the conditions of heat exchange and mass transfer between the heated bubbles and the VV surrounding it.

It is known that if we ignite nitroglycerine at a lowered pressure in a pipe with diameter 3—4 mm and, while conducting the experiment in an enclosed volume, we allow the pressure to be increased, then at 300—400 mm of mercury the burning dies out due to agitation of the liquid, that so strongly cools the gases that burning cannot be propagated. The increased inflow of nitroglycerine into the zone of burning extinguishes it. Under greater pressures the same phenomenon may result not inextinguishment but in the generation a detonation, and under a further increase of pressure burning can be observed anew, but with a significantly high speed. Experiments of the Swedish investigator Johansson have shown that analogous phenomena are observed, when liquid, containing gas bubbles, is subjected to impact.

Essential are the further conditions of the process, which are reflected in mass transfer and transmission of heat from heated gas in VV and in its possible additional heat-up as a result of friction. Therefore an adiabatic heat-up of the gas bubble is not the only factor, that determines the outcome of the experiment.

From experiments, showing an absence of noticeable effect of pressure on generation of the flash, it is impossible to conclude that this pressure cannot have a considerable influence on the generation and propagation of an explosion on impact. This occurs whether the explosive reaction is in the form of burning, which according to the investigations of Bouden usually occurs in the beginning, or in the form of explosion -- in both cases pressure plays a very important role. The critical diameter or dimension, starting from which the propagation of explosive transformation becomes possible, depends greatly on pressure. A sharp lowering of pressure during burning, as a rule, leads to its extinguishment. Therefore the magnitude of pressure and the duration of its existence are important factors in the generation and development of an explosion on impact.

Heat-up of gas bubbles is not the only method by which mechanical energy on impact can change into heat. Apparently, under conditions of an impact on a drop-hammer and in many other cases, the flow of VV has a decisive value and appearing with this, the local heat-ups due to internal friction. These methods of generating an explosion were studied in investigations by N. A. Kholevo, showing that in many cases on impact an explosion generates, if there is a possibility of flow of VV, and it does not occur if this possibility is absent. A number of paradoxical phenomena -- the influence of inert impurities, the increasing fluidity and sensitivity of low-fluidity VV and the decreasing sensitivity of high-fluidity VV, the dependence of results of impact on presence of a groove in the sleeve of the instrument, the increase of frequency of explosion with a lowering of temperature and other phenomena are explained, naturally based on the main concept of N. A. Kholevo -- no flow of substance, no explosion.

Works of German and Swedish investigators published in 1958 lead them to conclusions about the role of VV flow during the triggering of an explosion by impact, which ten years earlier were made by N. A. Kholevo. Apparently, this way of generating heat-up on impact actually is the most important.

The investigations of Prof. Bouden on the burning and explosion of separate crystals of explosives are of great interest. The Macroprocess of burning, the rules of which interest us directly, represents a combination of processes in separate crystals in combination with their mutual effect. The study of elementary processes undoubtedly will help us understand the rules of macroprocess. Especially interesting is the spontaneous splitting of crystals observed by Bouden, it occurs even during their slow decomposition and undoubtedly plays an essential role in the burning and its transition into explosion.

Indeed this last phenomenon is undoubtedly combined with a sharp acceleration of the process. Investigations have shown that pressure by itself increases the burning rate relatively weakly. Therefore, the most probable means of accelerating of gas formation and pressure increase during burning is to increase the burning surface, which can generate as a result intense fragmentation of burning particles.

A study of the ways of dispersion is one of the very interesting problems of the theory of explosion and we trust that Prof. Bouden's investigations in the laboratory will introduce in the future much that is new into this question.

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Pages 37 - 52

K. K. Andreyev

3. Concerning the Question of Factors Stipulating the Appearance of Explosion on Impact and Friction and About Methods of Appraisal of Sensitivity of Explosives (VV) To Mechanical Effects

On factors stipulating appearance of explosion on impact and friction

Explosion of VV can be caused by different effects -- in particular heating, impact and friction. The sensitivity of an explosive to each of these effects is an important characteristic, often limiting its area of application and determining the production condition of the VV. The measures of the sensitivity of a VV to given influences are obviously definite critical indices the transition through which leads to explosion. However answering the question of just what kind indices of one or another influence can serve as such a measure is far from always simple and clear, if the mechanism of excitation of explosion is unknown. We will explain by this example. It was possible to assume that sensitivity to thermal influences is characterized by a certain critical temperature for a given VV [3], similar to the melting temperature. The theory of thermal triggering of explosion, applied also in principle to the condensed VV, showed, however, that not only the temperature, but also the dimensions of a heated charge determine the possibility of the triggering of an explosive transformation. With a fuller description of the phenomenon it is necessary to consider also the duration of heating, since for many VV the course of the decomposition reaction, even in isothermal conditions is self-accelerating. In experimental determinations for one and the same VV, it is possible generally speaking, to obtain strongly varying values of flash temperature.

The cause of these distinctions, however, can be, as a rule, explained on the basis of the above shown considerations; if they are taken into account during the setting up of experiments, then the value of the flash temperature (and also its delay) is sufficiently well reproduced and the scattering of experimental data is relatively small. Therefore the characteristic of the sensitivity of a VV to thermal influences in its simplest form (flash temperature), is sufficiently definite in magnitude and physical concept.

Matters are considerably different regarding sensitivity to mechanical effects --in particular to impact. Results of experimental determinations in their usual expression (frequency of explosions at a given energy of impact) differ very strongly for different investigators in absolute value; with this the change in frequency-- from absence of explosions to absence of refusals--can occur in a very significant range of variation in the energy of the impacts commensurable with its absolute value. In connection with this even in strictly controlled laboratory conditions the determination of sensitivity of a VV to impact is built on the statistical principle, i. e., on the determination of the frequency of explosions, although it would have been possible to visualize a similar flash-temperature critical height (energy) or other critical impact parameter. With such a determination, even by one and the same investigator, the variation in the results of a parallel series of experiments (usually every series includes 25 experiments) is ordinarily very significant; this is observed in spite of the fact that the conditions of the experiment which supposedly can influence the results are maintained constant within the limits possible to the experimenter.

Such a relatively low definitiveness of the sensitivity of a VV impact is stipulated, apparently, by a series of causes. One of these causes is the complexity of the phenomena, in any case much greater than in thermal excitation of explosion which in this particular form is only one of stages of excitation of explosion by impact. The complexity of the phenomenon is reflected in the fact that at reports stages of its development the same factors can sometimes act very differently, favoring one stage and suppressing another. Depending upon conditions the action of separate factors can, besides this, change not only in magnitude, but also in direction. We will explain this, considering the development of explosion on impact in accordance with the presentations of N.A. Kholevo [4].

As a rule, the action of impact in exciting an explosion leads to incomplete compression of the explosive, in consequence of which a fast flow of the VV arises. Owing to the irregularity the flow friction appears between layers of the explosive[1] and, as a result of this, local heat-up[2], strongest in zones of the highest gradient of speed of flow, also appears. If dimensions and temperature of the seat of the heat-up are sufficiently great, then ignition and burning occur, passing with favorable conditions to explosion. Besides the dimensions and temperature of the seat, pressure also can affect the possibility of triggering explosions; the higher the pressure and the longer it is maintained, the easier is the VV ignited; pressure affects also the transition of burning to explosion.

One of the sources of the instability of experimental conditions and results with impact, since it is realized on drop hammers,consists in the possible non-parallelism of the colliding surfaces and in some misalignment of the upper roller, leading to differences in pressure and flow speed in various parts of the charge. Besides this the tablet of VV itself, cannot be mechanically wholly uniform. Experiments with inert plastics in instrument No. 2 [4] showed that during impact of a drop hammer on a thin cylindrical tablet form, the tablet is usually distorted in a radial direction, i. e., deformation occurs unevenly; further more, the transition from heights at which the dimensions of tablet do not change to heights, where deformation is observed at every experiment requires a significant--more than twofold--increase in the height of fall of the load. The state of surface of rollers has a large influence. Even in laboratory conditions, where the degree of mechanical processing and of surface cleanliness is controlled large variations in

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[1] Appearance of heat-ups is possible as a result of external friction between the VV and the surface along which it is transferred, if the friction between them is sufficiently great. The friction of alien refractories and hard particles contained in the VV with each other or on the surfaces between which it is included, also can lead to local heat-ups and explosion.

[2] The fact that micro--, but not macro- heat-ups play a decisive role shows the significant influence of crystal dimensions on the frequency of explosions of even such low-melting VV as nitroglycerine. If a charge, subjected to impact, was melted completely and then detonated in liquid form, crystal dimensions could show no influence.

the frequency of explosions are observed during tests from series to series of experiments. These variations clearly surpass the possible limit of accidental deflections and show a systematic character.

Experiments with artificial application of small layers of lubricant on the roller surfaces showed that frequency of explosions of hexogen (in instrument No. 2) with this increases by two or more times. However a high frequency of explosions was also observed and with certain methods of washing the rollers with the aim of removing the lubricant from them. Apparently, a change in the surface state of the metal has an influence on the adhesional durability of their contact with VV. This in its turn changes the velocity profile in the flowing layers of the VV, tending in given conditions in the direction of increasing the possibility of appearance of local heat-ups.

It is obvious that in industrial conditions methods of the purification or processing of surfaces touching a VV ensure to a lesser degree the stability of its state, for which reason large variations in explosion frequency are still possible.

If tests are conducted in instrument No. 1, it is conclusive that the most strained stage of deformation is the flow of the VV in the gap between the roller and sleeve. The magnitude this gap can change by two times, depending upon whether the roller occupies a central position in the sleeve or is pressed to one of the sides.

Thus in instrument No. 2, and still in a large degree in No. 1, the first mechanical stage of phenomenon proceeds very unsteadily. This variability can be strengthened by two circumstances. If the substance has a relatively low melting temperature, then in those places where flow starts; local melting occurs; this will lead to a sharp increase in the fluidity of the VV, since the melt serves in its own way as a by lubricant[1]. Further, we usually are concerned with substances (powder or thickened melt), including gas (air) bubbles that during impact are compressed and serve as seats of temperature increases melting and local strengthening of the flow of the VV[2].

Variations in the temperature and dimensions of seats of heat-up appearing at impact are apparently, one of the main causes of the variability of test results. About this it is possible to judge by the fact that during homogeneous heat-ups, the values of the characteristics of the triggering of explosions (temperature or delay of flash) are subject to much smaller variations.

In the triggering of an explosion by impact, the variability of the conditions in the first place, pressure also acts on the development of the focus of ignition. Whether the heat-ups appearing at a given temperature can cause explosive transformation, depends in many respects on the dimensions of the seat[3]. In large seats, other conditons being equal, this transformation is developed more easily than in small ones, owing to the general cause that generation of energy of a reaction, ensuring the propagation of the latter, occurs in a volume proportional to the cube of the linear dimension of the seat of heat-up and heat loss-through the surface and proportional to its square.

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[1] Fusion can set in also in the stage of decreasing pressure during impact. It is known that with an increase in pressure, melting temperature is increased. Therefore, if dislocation of layers of the VV starts at very large pressures, then at first, in spite of the increase of temperature, the VV will be in the solid state. With a decrease in the impact pressure, the melting temperature is lowered, fusion sets in, and the flow is strengthened correspondingly.

[2] On the role of gas pockets in VV and of air entrapped during impact, see also pp. 36, 99 of this work.

[3] It is known that in the usual conditions of the triggering of flash of a VV by heating, it occurs with a significant delay, stipulated by the chemical development of the self-accelerated exothermal transformation. With those high temperature and transient heat-ups, appearing during impact, chemical development of reaction hardly succeeds to proceed to a significant degree and this side of phenomenon does not attain an essential value.

The number of heat-up seats appearing depends on the homogeneity of the actual VV, as do the conditions of its flow. In a very uniform VV, even chemically highly reactive, a case is possible when with a relatively weak effect a large number of small, partially developed heat-up seats appear, whereas with significant mechanical heterogeneity of the explosive and at a given speed of energy absorption, large self-developing seats are generated more easily, that is, with greater probability.

Since the homogeneity of substance is never full or identical, this also constitutes a source of variability, absent at least in such a sharp degree. During the excitation of an explosive transformation by an even heat-up, when the condition of disturbance of equilibrium between heat-imput and heat-output obtains for the entire volume of the VV.

As the second stage one should consider the appearance and development of burning in at least one of the seats of heat-up. Frequently this stage is discussed from the position of the theory of thermal explosion. This is hardly the most successful and exhausting variant of approach to the given phenomenon.

In the theory of thermal explosion one usually considers a certain charge having definite dimensions and temperature, and it is established at which mutually connected values of these parameters the heat input becomes larger than the heat output. Without even mentioning that during impact the especially difficult to a define form and dimensions of the seat of the heat-up and also the distribution of temperature in it are completely undetermined, their interconnection can be considerably different than that which takes place during the usual thermal explosion. In the theory of thermal explosion, the speed of heat release is expressed in dependence upon temperature by the relationship

$$Q_0 B e^{-E/RT}$$

where Q_0 is the thermal effect of the transformation of a unit of volume of VV into its products, which are obtained during a low-temperature reaction of disintegration, and the remaining letters have their usual value. As is known, with this reaction an organic VV will usually release only part of its potential energy. Under the conditions of impact Q_0 is not constant, but can noticeably, and sometimes sharply, depend on pressure and temperature, increasing with them at the expense of the passage of the transformation reactions of the VV to a completion.

Further, in those explosives in which the main part of the thermal effect gives a reaction in the gas phase, the burning rate strongly depends on pressure; in this case the development of the seat of the heat-up here is implied a heat-up bringing the VV to that **state** of transformation, which occurs in the gas phase with speed depending on the pressure is determined in significant measure by pressure. In the theory of thermal explosion of a condensed VV, the effect of pressure usually is not taken into account, on the known basis that since, for example, the flash temperature is almost independent of pressure [5]. It is possible, therefore, to consider a thermal explosion only as a possible initial stage of a chemical transformation on impact, especially if the heat-ups are weak. The triggering of burning on impact is very correctly interpreted from the positions of contemporary proposals on the ignititon of VV, according to which a condition of stable burning is the equality of thermal flows from combustion products to a heated layer, moving with the burning rate, and from the heated layer to unreacted substance.

Let us remember that parallelism is not observed between impact sensitivity and flash temperature, which in essence is itself a thermal explosion, only in known **measure** to complicated chemical development of reaction. At the same time such parallelism exists in reference to inflammability, especially if the latter is taken at increased pressures, corresponding to conditions of the triggering of explosion on impact.

There is still another essential argument against the usual treatment of the triggering of an explosion on impact as a thermal explosion, at least for secondary VV. The critical diameter for burning of these substances at atmospheric pressure is many times greater than the thickness of the layer of VV used in sensitivity tests. Therefore even if there appeared a thermal explosion with the maximum dimension of the seat equal to the thickness of the VV layer, and with a maximum temperature equal to that of burning, still would not lead to ignition at atmospheric pressure. It is necessary in connection with this to consider the effect of pressure, as does the theory of ignition.

Incidentially the consideration of the triggering of an explosion on impact from positions of inflammability gives a natural and simple explanation of cases of so-called incomplete explosions frequently observed during experiments; these cases usually represent damping due to pressure drop or failure of burning to develop. This explanation, in reference to the second case, is easy to illustrate by the following simple experiment. If one touches a charge of powder with an incandescent wire and quickly removes it, the charge will flash at the point of contact, but will not ignite; the seat of thermal explosion created by the wire is too small to heat-up a layer of the thickness necessary for stable propagation of burning. Thus a condition of thermal explosion can obtain without the triggering of burning, if the volume, in which the thermal explosion occurs, is too small.

Such a varied development of chemical processes on impact, including local chemical transformation (that can be completed by a thermal explosion) and self-propagated transformation in form of burning and explosion, developed to completion or interrupted at various stages of its development, extraordinarily hampers the experimental characterizing of the sensitivity of VV on impact. We evaluated the results of a individual test only by explosion or absence of explosion, at the time when it would be necessary to describe this result and at that quantitatively from at least three sides -- the appearance of heat-ups and seats of chemical reaction, their growth stature in form of burning, and the transition of the latter to explosion. With this there can also be the various numbers of seats and the dimensions and the location in the charge of each one, on which the result of process also depends.

This side of question presents direct practical interest. The most dangerous explosives are those in which seats of disintegration appear and propagate easily. If we will imagine two VV, in one of which seats of disintegration appear easily, but propagate with difficulty and vice versa, one in which they appear with difficulty but propagate easily, then, depending upon the conditions, in which deformation is produced, either the first or the second substance may be more dangerous. With the existing test of method, we were deprived however, of the possibility of analyzing the triggering and development of the explosion.

The experimental evaluation of the appearance of seats of disintegration, especially if they do not develop to burning, is very subjective; sometimes there is a small change of external form of the VV or its color (browning, blackening), and by these characteristics it is not always possible to distinguish fusion from decomposition; in another case the odor of decomposition products or a local scattering of material appears. It is necessary to add that it is sometimes very difficult to distinguish the scattering, appearing in a seat of chemical reaction from scattering due to purely mechanical causes. Thus, for example, with the removal of pressure strongly compressed hexogen is usually spontaneously scattered, sometimes so intensely that an explosion appears at the same time.

A second characteristic of the process--the development of burning on impact--also is not estimated quantitatively, although test results in this relation can be considerably different, i. e., burning can be propagated on the whole charge or limited to a part or parts of it, or can be full or incomplete. Finally, it is difficult to establish whether the transition of burning to explosion had a place during a test, since we can judge the presence of explosion only by sound, which can appear also as the result of burning under high pressure.

The only direction known at the present for the quantitative approach to the appraisal of the considered phenomenon, although also having an integral character, consists in the determination of the degree of the completeness of the explosion according to the quantity of gases formed during a given experiment. Chemical methods of quantitative appraisal of appearance and development of seats of reaction are complicated.

In connection with the very low reproducibility of test results, certain investigations expressed opinions on the unfitness of the drop-hammer as an instrument for the study of sensitivity of VV. It is scarcely possible to agree with such opinions, at least if speaking of the determination of sensitivity as a practical characteristic of VV, since those effects that influence the results of tests on a drop-hammer may also be manifested during work with VV in production.

However, this conclusion by no means excludes the expediency of the use for the study of VV of such simpler methods as the determination of sensitivity to friction or to transmission of detonation at a distance. We will dwell in a little detail on the last test. On the basis of experiments with a series of secondary VV, the author for a long time pointed out the parallelism in their sensitivity under impact and the conditions of transmission of detonation at a distance [1].

Recently this parallelism was confirmed anew and expanded (A. Ya. Apin), and besides it was shown that a noticeable similarity is observed between results of tests on a drop-hammer and on transmission of detonation, even with respect to role of such characteristics of VV as crystal dimensions.

However, sensitivity to transmission of detonation characterizes only one, although perhaps the most important side of triggering of explosion on impact namely, the inflammability of the VV during momentary pressure[1] and the action of gases at high temperature and pressure. The role of the stage of heat generation during mechanical deformation of a VV, in other words the stage of formation of seats of high temperature, here is decreased and those peculiarities of the substance, in particular its fluidity[2], that in the biggest measure affect just on this stage are erased. The difference between sensitivity to impact and to friction is in these test conditions, impossible to grasp. In their turn certain peculiarities are developed, specific for a given form explosion triggering--for example, a sharp influence of the initial density of a powder, which operates to a much lesser degree during impact. The one-sidedness of test on transmission of detonation is still more graphically revealed in the case of charges of smoke-

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[1] We will note incidentally, that the speed of deformation during transmission of detonation and during triggering of explosion by impact differ strongly.

[2] It is scarcely possible to doubt that flegmatization of azide of lead by paraffin decreases distance of transmission of detonation; during tests on a drop-hammer it, as it is known, increases the frequency of explosion.

less powder, which as it is known, poorly transmits detonation at a distance, possessing at the same time high inflammability and sensitivity to impact.

Therefore, testing of transmission of detonation is quite useful during the appraisal of sensitivity to impact, especially if substances close in physico-mechanical properties are compared, when distinctions in sensitivity impact are determined not by the latter, but thermokinetic properties of the VV. However, as is clear from the above, receptivity to transmission of detonation does not always exhaustively characterize the sensitivity of a VV to impact.

The poor reproducibility of results of tests on a drop-hammer naturally greatly hampers accurate appraisal of the effect of those or other characteristics of a VV on its sensitivity.

However, in a number of cases, including cases having direct practical interest, such appraisal is possible.

We will recall first of all the results obtained by N. A. Kholevo [4] and the interpretation he gave them. This investigator showed that if a VV possesses great fluidity, the highest frequency of explosions is observed under the conditions of impeded flow, which can be obtained in instrument No. 1. During tests in this instrument relatively large stresses appear in VV, in consequence of which the coefficient of internal friction increases and are strengthened correspondingly the heat-ups formed in the substance during its flow. On the contrary, in tests of VV with low fluidity the highest frequency of explosions is observed under conditions of relieved flow, realized, for example, in instrument No. 2.

The degree of complexity of flow in instrument No. 1 depends naturally on the magnitude of the gaps; this affects the frequency of explosion. As experience shows, the maximum frequency of explosion is obtained at various gaps for different VV therefore, the "optimum" gap magnitude cannot be predicted beforehand. N. A. Kholevo applied even more vigorous conditions of flow during tests of liquid VV, placing them in a cup of fluid metal for example lead (see page 8).

It is possible to relieve the flow of substance in instrument No. 2 by decreasing the diameter of the rollers (at the same specific energy of impact) or the diameter of the charge. Incidentally, deformation conditions corresponding to those that take place in instrument No. 2 can be realized in instrument No. 1. For this it is above to arrange the batch of VV in the form of a tablet or a small pile, with a diameter less than that of the rollers. The free circular part of the space between the rollers and will, during impact, play the role of the groove of instrument No. 2.

V. S. Kozlov proposed an instrument with slightly rounded transition from face to cylindrical surface, combining the condition of instrument No. 1 and 2. In this instrument are realized in the initial stage, the conditions of instrument No. 2, i. e., relieved flow, but later, when the free space, small in volume, is filled VV and the latter starts to be pressed through the gaps between the rollers and the sleeve--the conditions of instrument No. 1. Thus in V. S. Kozlov's instrument the sensitivity of a VV can be shown in known degree independently of its fluidity--this instrument, as it were, combines the tests in instruments No. 1 and 2. In this consists its advantage, but simultaneously a drawback, in that the precise kind of conditions --stress or relieved flow--the VV is the most dangerous remain unknown. We will add that the idea V. S. Kozlov has been for a long time embodied in reality in the form of that instrument which is applied in accordance with All-Union Government Standard GOST 2065--43. In this instrument, thanks to the presence of faces on the rollers, there is an annular space, playing the role of the groove of instrument No. 2; since the volume of this groove is small as compared to the volume of VV, then in the future it is pressed through the gaps between the rollers and the sleeve canal, similarly as it occurs in instrument No. 1.

In the former, a caste stamping instrument applied by us, the piston did not have faces; the appearance of the latter was combined with transition on bearing rollers, which have these faces . The authors of GOST, allowing the use of rollers with faces, scarcely considered the possibility of a strong effect of these faces on the frequency of explosion of certain (low-fluidity) VV, or all the more so, imagined the physical significance of this effect. It is possible that certain differences, appearing in their own time in the appraisal of the sensitivity of various VV like flegmatized hexogen with aluminum, whose sensitivity was estimated to be lower than the sensitivity of trotyl, were stipulated specifically for the application in one case of instruments without faces but in another, with faces, in ignorance of the role and strong effect of the latter on test results.

In any event, a test in an instrument according to the GOST gives usually an approximate presentation of the sensitivity of a VV; tests in instruments No. 1 and 2 defines more accurately this question: in what conditions--relieved or hampered flow--is an explosive, in accordance with its fluidity, most inclined to explosion on impact.

One should to add that although the fluidity of a VV can place the strongest imprint on its behavior on impact, the kinetic and thermochemical characteristics of the VV in no way lose their role, which, when they are sharply distinct, can be determining.

The relationship of these two factors of sensitivity is very graphically explained by N. A. Kholevo; if we had two VV, identical in physicomechanical properties, then sensitivity would be determined only by their chemical-kinetic and thermal characteristics. If, however, the physicomechanical properties actually differ then the sensitivity (frequency of explosion) of the VV depends also on them. The less distinction of physical properties of compared VV, the greater is the degree to which their sensitivity is determined by kinetic and thermal characteristics.

In its turn, the role of physical factors would be discovered in pure form, if we had VV identical in chemical-kinetic and thermochemical characteristics but differing in physical properties. Incidentally , a case we have near to this if one and the same VV can be tested under identical external conditions in different aggregate states. Such a test has been realized, for example, on nitroglycerine capable of strong supercooling; it showed, as it is known, an essential distinction between the frequency of explosions of liquid and solid matter.

From the above it follows that for a full and differentiated characterization of the sensitivity VV to mechanical influences it is necessary to make a complex of tests, establishing role of chemical-kinetic and thermal, as well as physical factors in the process of triggering explosion. The first, in known measure, can be integrally characterized by the inflammability of the explosive at increased pressures, and also by its susceptibility under the conditions of transmission of detonation of a distance, and the second --by tests on a drop-hammer in instruments 1 and 2, and also by the determination of sensitivity to friction. In the last test, the conditions of friction are fixed in a larger measure by the experimenter, than in instruments No. 1 and 2, where they are determined primarily by the fluidity of the VV.

At the present time, complex tests of VV for sensitivity with a series of causes are not carried out. However, even single tests on a drop-hammer reveal a number of regularities meriting attention.

Thus, during investigations of VV homotypic in chemical structure, a significant effect of the melting temperature on test results was observed. If the melting temperature is relatively low, then, as was already noted, the melt formed at the beginning of flow on the surface of particles plays the role of a unique lubricant, lowering the coefficient of friction and decreasing the frequency of explosion in relieved conditions of flow, for example, in instrument No. 2. On the other hand, in instrument No. 1 the frequency of explosion can increase. However, not only absolute value of the melting temperature, but also its proximity to the temperature of fast decomposition, in other words the speed of decomposition of the melt formed. If this speed is great, then the "lubricant effect" is weakened and the frequency of explosion is high also in conditions of relieved flow[1]. Under conditions of hampered flow melting usually is absent and the frequency of explosions is lower part.

Interesting is the behavior of systems including a low-melting base and relatively high-melting low-fluidity powder, sensitive under conditions of relieved flow. The sensitivity of such systems, especially with large contents of the high-melting component, can be determined in the first place by the latter's own properties, i. e., it appears high. The properties of the fusible base are less essential. This is especially evident for mixtures of azid of lead with paraffin; in fixed test conditions, when the frequency of explosion of the azide is near to zero both in instrument No. 1 and in instrument No. 2, it is abruptly increased in the presence of paraffin.

The decisive factor determining the increase in the frequency of explosion in these cases, is, obviously, the increase in the fluidity of the substance and possibility stipulated by this friction between particles of the hard high-melting component. The possibility of the propagation of explosive transformation during the addition of the low-melting substance can stand, but in the conditions of the given example, undoubtedly becomes lower; but it does not limit the triggering of explosion in the given case.

If, however, the low-melting component in the mixture is relatively great

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[1] One can expect that the sensitivity of eutectic alloys of low-fluidity VV will be, in known conditions, lower than that of their component parts.

and it is chemically relatively inert, then its flegmatizing action on the stage of development of explosion can be significant as is observed, for example, in a 50% "alloy" of hexogen with trotyl.

On the other hand, here the change of physical properties (increase or decrease of fluidity) of the system can play an essential role.

On the Appraisal of Sensitivity of VV to Mechanical Effects in Reference to Practical Conditions.

With variations in experimental results for one and the same substance, with a great-and different for various VV--dependence of frequency of explosions on test conditions (construction and dimensions of instrument, thickness and diameter of charge, magnitude of gaps, etc.) arises the question of how, then, to estimate sensitivity of explosives in reference to the demands of practice. Here it is appropriate to quote those conclusions, arrived at by American physical chemists in summing up attempts to determine sensitivity [6].

"As a result of investigations, however, it was determined, -- and this is a discovery of significant practical importance--that it is impossible to find such a characteristic as a definite mechanical sensitivity of an explosive. Indeed, by change in test conditions, it is possible to change even the order of mechanical sensitivities of explosives. Thus laboratory tests are not in a state to establish the absolute danger of industrial operations, producible upon explosives. In the best case, the application of various tests can give only warning that a new VV is in general more dangerous than another, already in use; maybe this test will be able to give also certain indications relating to especially dangerous conditions."

These conclusions are in essence analogous to those earlier arrived at independently by N. A. Kholevo, uncovering also the physical concept of the variability of sensitivity.

It is necessary to add however, that if for any VV, changing the corresponding test conditions, either very high or very low frequency of explosion can be obtained. then for substances with close physical properties (for example, for many trinitrocompounds of the benzene series) under ordinary test conditions, for example in an instrument conforming to All-Union Government Standard /GOST/ 2065--43, one can obtain an approximate comparative characteristic of sensitivity, reflecting in such a case their kinetic and thermochemical properties.

The question arises, however, of the extent to which results of such, or complex, /tests/ can be transferred to the conditions of processing and application of VV.

The answer to this question is very complicated, in the first place due to insufficient knowledge of the character those influences to which a VV is subjected in practical conditions. Thus, experimentally proven presentations on the mechanism of the triggering of premature explosions during a shot, sudden explosions during compression boring, etc., are not clear. It is of little help to turn to practical processes of decreasing the sensitivity of VV. Such a position is dictated first of all by the fact that broad experimenting in these questions has not been realized, since every experiment on a full scale, if it is, ends in an explosion, is very expensive. Usually a negative conclusion on the possibility of the application for a given VV of one or another technological process or method of use is founded on single explosions having a place in practice, which could be random.

To decrease the sensitivity of VV to mechanical effects, the practice knows two main processes of flegmatization; one consists in the application of alloys, including a VV with great energy of explosion and high sensitivity and a VV with lesser energy of explosion and low sensitivity; as examples one can cite alloys of picric acid with /dinitronaphthalene/ and of TEN with trotyl. In this case the decrease in sensitivity occurs mainly at the expense of lowering the general reactivity of the VV and its explosion energy as compared to the most sensitive component.

However, another method of flegmatization is widely applied, in which particles of a highly sensitive VV with a high melting temperature are enveloped by a layer of nonexplosive viscous substance; a typical flegmatizator is paraffin. As a flegmatizator can also be applied a low-sensitivity low-melting explosive. This role is played, for example, by trotyl in "alloys" with hexogen. It is possible to propose that low-melting viscous additions play the role of lubricants during flow of the VV caused by impact or during friction and decrease those heat-ups, that would appear in their absence. This action of theirs is analogous to the action of melt formed on the surface of particles of a low-melting VV during their fast deformation.

Side by side with this, flegmatizors undoubtedly play also the role of improving formability, in particular pressability, of the explosive. This makes less dangerous and therefore technically feasible its pressing, since in the case of application of a flegmatizor higher density will be attained with smaller pressing pressure; besides, those stresses and tangential forces efforts, that would be inevitable in the achievement of high density of charge by pressing unflegmatized powder do not appear. A denser charge, with other conditions equal, is more difficult to deform.

We will recall in this connection that during tests on a drop-hammer, the presence of a flegmatizor often increases the frequency of explosion. This occurs in those conditions, where the absence of explosion of an unflegmatized VV is stipulated by him its insufficient (for given conditions of action) fluidity. Under slow actions (pressing) the same increase in fluidity have the reverse effect. Increased fluidity of a VV, in particular its ability to be melted without essential decomposition, hampers, generally speaking, the triggering of explosion under such relatively slow actions, as the VV is subjected to in the process of boring and pressing. Thanks to the fluidity those local stresses, which can appear in a VV during these processes are removed. Due to this, in the first place, strong local heat-ups do not appear; secondly, the reaction is not developed in seats of heat-up even if they appear.

It is known that arming of ammunition by pugging of trotyl is relatively safe. It may be possible to explain this by the relative chemical inertness of trotyl. However such an explanation is hardly sufficient, since the significantly more reactive amatols whose frequency of explosion during tests on a drop-hammer is much greater than that of trotyl, can also be pugged. Obviously, therefore, the essential factor of the danger of pugging is fluidity, in particular the fluidity stipulated by the possibility of melting without decomposition. If a VV does not possess such significantly expressed fluidity, then large stresses of movement, if they appear, cannot to be softened and will call forth critical heat-ups.

However, too large a fluidity of a VV such, for example, as that possessed by low-viscosity liquids, can with known prerequisites increase the possiblilty of explosion. We will imagine that is realized an impact a refractory metal against a metal covered by a layer of explosive liquid which, owing to its low viscosity does not render essential resistance to the approach of the impacting surfaces. In this case especially, if the angle of collision is at least a little off the perpendicular, the movement and deformation of the metallic surfaces, as is known, leads to the appearance of strong local heat-ups. If a VV, for example nitroglycerine, possesses great reactivity and is capable under high pressures of burning even as a film, then it can be ignited and detonated from friction of metal against metal. This explosion then is **transmitted** to the remaining mass of the VV not subjected to a direct impact. Low viscosity can, besides, relieve the triggering of explosion due to compression of gas bubbles.

If the viscosity of nitroglycerine is increased, for example, by dissolving in it nitrocellulose, then both these possibility of triggering of explosion are realized with more difficulty.

Thus too low and too high fluidity of a VV can at known conditi chanical effects favor the triggering of explosion.

In conclusion we will touch that somewhat scholastic aspect of the problem, in which it was recently set by certain investigators. It is a question of attempts to consider sensitivity as a certain absolute constant of a VV, stipulated only its chemical structure. With this it was indicated that the physical properties, whose role of is underlined by N. A. Kholevo and associated investigators, are stipulated by the chemical structure of the substance.

Proponents of these opinions forget that there are in general no absolute properties of a substance, that all properties in greater or lesser measure depend on conditions, in which the substance is found. Therefore only by force of habit[1], appearing in those times when the sensitivity was a thing in itself, when its physical meaning was not known, can be explained the tendency to attach to every VV, a label with the number of its sensitivity and on this basis to consider the problem of the knowledge of the latter to be completed.

Further, if a chemist, knowing the composition and chemical structure of a VV, could quantitatively characterize its physicomechanical properties, then it would be possible to consider these properties, which are important factors of sensitivity, not directly but through their functional dependence on composition and structure. Along with this we do not calculate physicomechanical properties according to composition and structure, but establish them by means of direct

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[1] In reality, we know that the sensitivity of a VV to detonation depends on the crystal size and on the density of the powder, but this no longer surprises us and we do not look for some absolute sensitivity to detonation. Just as few are the basis for and seeking in reference to sensitivity of a VV to impact. Dependence on conditions of action is by no means a peculiarity of these or other characteristics of a VV. In the resistance of materials we speak of rupture, pressure, and shear strength, and this does not cause surprise and does not force a search for some single absolute strength, although such a concept would be incomparably simpler to connect with composition and structure. As a third example it is necessary to recall the concept of brittleness; its convention, the dependence of brittleness for example, on the speed of deformation, is well-known.

determination. Besides this, the physicomechanical properties of given chemical compound also are not an absolute constant of it and therefore the sensitivity of a VV cannot be constant. That it is not, it is possible to illustrate by many examples. Thus, naturally, the sensitivity of one and the same compound of the gaseous liquid, and solid states differ, the sensitivity of solid matter can depend on dimensions of crystals. It is known that different crystallographic modifications of a certain VV also differ in sensitivity. Finally, external conditions, which it is in no way possible to include in the concept of chemical structure of a tested substance, also have an effect on sensitivity. Sensitivity to friction can be distinguished from sensitivity to blow impact; it depends, in particular--and this dependence is explained by Bouden[2]--on the temperature of melting of materials, between which friction is realized.

Thus sensitivity is variable, depending on the properties of the VV and on external conditions, including conditions of deformation. Appears, however, the question: is it impossible to express this dependence completely, or at least partially by a quantitative formula? In principle this is possible. Practically, in view of great complexity of the process, attempts in this direction (including the attempt of L. V. Dubnov, Evans, and other investigators) have had no success. Simultaneously, separate determining characteristics of phenomenon are clear; this --from a number chemical-kinetic and thermal properties--the thermal effect of reaction, the thermal capacity and conductivity of the VV, the specific velocity of heat release in its dependence on temperature, the burning rate depending upon pressure (the effect of these factors is partially united in inflammability, and also in the magnitude of the critical diameter of the charge); from physicomechanical properties and conditions of deformation--coefficients of internal and external friction in dependence on pressure and temperature, degree of homogeneity of the VV (in particular, the presence and dimensions of gas pockets), pressure and speed of its change in time, initial temperature, temperature of melting, shell, dimensions of holes in it and other characteristics of deformation conditions.

Conclusions

The triggering of explosion during mechanical effects on an explosive is stipulated by the appearance in the VV of local heat-ups. These heat-ups can be formed during nonuniform flow of the explosive, during compression of gas bubbles in it, during friction of particles, refractory impurities, or hard surfaces, one of which is the explosive. The development of a chemical reaction appearing in seats of heat-up to burning and explosion depends on their temperature and dimensions and on pressure.

Inasmuch as the triggering of explosion is determined by many factors, the most important of which are chemical-kinetic and thermochemical characteristics of the explosive, its physical properties (fluidity), and the conditions of deformation, the sensitivity (frequency of explosions) under mechanical effects can vary in wide limits.

For an integral appraisal of sensitivity it is necessary to determine a complex of properties of the explosive—the frequency of explosions on a drop-hammer in instruments No. 1 and 2 and during friction tests and also the ability to perceive and transmit detonation at a distance, and the critical diameters of the charge during burning and during detonation. Besides, it is impossible to forget that the real danger of triggering of explosion under mechanical effects will in strong measure, depend also on the conditions of these effects determining the possibility of flow of the explosive and the appearance with this of local heat-ups, and also on the maintenance of pressure favoring the development of the initial transformation to explosion.

This article was written in 1956. Certain considerations developed in it, originated from the conversations with N. A. Kholevo, whom author in this connection remembers with deep gratitude.

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Chapter 1, Article 4, Part 1

Pages 53 - 61

K. K. Andreyev and Yu. A. Terebilina

4. About the Triggering of an Explosion on Impact and Methods Describing the Sensitivity of Explosives Mechanical Effects

The Mechanism of Triggering an Explosion on Impact

By the term sensitivity of an explosive is understood the capability of latter to react to external effects with the generation of burning or explosion. This capability can be expressed more or less by factors, determining the sensitivity of explosive to mechanical effects. They are its properties and the condition of the effects, that assure in the charge a creation of a seat of heat-up of sufficient temperature and dimension, and also the propagation and development of the transformation which had begun in it prior to the explosion. Together, these factors determine the danger of the generation an explosion, i. e. sensitivity of an explosive, under definite specific conditions. They can be divided into two groups: chemical in the broad sense of the word and mechanical.

Inasmuch as the first stage in time of the phenomenon under study is determined chiefly by mechanical factors, we proceed namely from them. At present it is universally recognized that an explosion under mechanical effects develops from local heat-ups, created by these effects. Ways of generating warm-ups can be various[1]. One of them is the nonuniform speed in the flow of the explosive. The second way is associated with existence of gas bubbles in the VV and the third — with local heat-ups from friction of solid alien particles

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1. See in present collection of articles, N. A. Kholevo (page 5), F. Bouden (page 27) and K. K. Andryev (page 47).

Note: VV stands for explosives.

or metallic surfaces of the anvil and firing pin of the device with a thin layer of explosive between them.

For the generation of local heat-ups not only the physico-mechanical properties of VV, but also conditions of the effect on it are essential. Thus, in order that explosive could flow during the compression, created by the impact, it is necessary that it is not enclosed on all sides, i. e., it should be given the possibility of flowing into a gap. Further, it is obvious that on the width and extent of the gaps, through which flows the explosive on impact, depends the pressure developing in it; on the magnitude of the same pressure in turn, depends the coefficient of internal friction and speed of flow, but through them also the intensity of the heat-up. The heat-up of gas bubble also depends on maximum pressure and rate of attaining the latter. Finally, if we are not concerned with the impact along normals, with which the genesis of the VV flow and, consequently, also friction is determined by the fluidity of explosive, but by a slipping impact, then the possibility of generation heat-ups in this case can be completely otherwise.

Thus, the generation of local heat-ups during mechanical effects on an explosive depends on very many factors, the combined effect of which quantitatively is difficult to take into consideration and even to evaluate. This circumstance introduces a large indetermination for the question on the circumstance whether or not a given effect results in the generation of a heat-up terminating with an explosion. In this respect, a mechanical effect as a means of triggering an explosion differs from many others, especially from the thermal. In the latter case, the association between the cause and effect is by far much more simple and therefore can be more readily evaluated.

The statement above, however, refers not only to mechanical aspect of phenomenon. The flash and burning of an explosive on impact proceeds under more complex conditions, in comparison with the ordinary conditions of corresponding experiments. The chief factors here are the varying pressure and small thickness of layer of explosive. It is known that according to theory Mikhelson - Zeldovich, the quantity of heat, that must be communicated to the surface layer of the VV charge in order to ignite it depends on the burning rate, but through it on the pressure. The larger the latter is, the less is this quantity. It depends also on heat conductivity of the explosive. Further, if burning begins but the pressure rapidly decreases, then it may cease, because the reserve of heat in the heated layer may not suffice for the burning to continue during low pressure. The critical diameter (more precisely the critical dimension) of the charge during burning under atmospheric pressure, as a rule, is much greater than under ordinary conditions of triggering an explosion on impact. Therefore, the burning, occurring on impact, can spread only in cases when a sufficiently high pressure is maintained.

Finally, as well as under ordinary conditions of a thermal explosion, the effect of the temperature itself attained at the seat of the heat-up, and the dimensions of the latter, is shown. Therefore, if we consider the chemical factors of sensitivity, then it is necessary to take into consideration also those of which determine the generation of a thermal explosion: rate of the reaction, caused by the heating, and its heat which, determines the temperature, being obtained in it. It is known that depth of the transformation of explosive, as a rule, depends on the pressure and, apparently, on the temperature. Therefore, it is not always easy to make certain those values of the constant of the rate and heat of the reaction, which actually are decisive in a triggering of an explosion on impact. In any case, it is impossible to identify them with data, obtainable during a gradual disintegration or during detonation.

Thus, from the chemical-kinetic standpoint, the triggering of an explosion on impact is much more complicated, than during its thermal excitation, for example, under ordinary conditions of determining the temperature of flash of the explosive.

A graphic illustration of this is the imcomparably greater constancy of results in determining the temperature or delay of flash in comparison with determining the characteristics of the VV sensitivity to an impact. In this respect, judging from observations on the character of deformation of nonexplosive substances on impact. The inconstancy of the results during triggering of an explosion on impact basically determine the mechanical factors, examined above.

In connection with complex character of the phenomenon and multiplicity of factors on which depends triggering of the explosion on impact, the practical value of characteristics of the sensitivity, obtained under specified conditions of the test, is limited. Indeed, if the mechanical conditions vary, but in practice they can vary very widely, then also the possibility of triggering of an explosion will vary. Therefore, in principle it is more normal for the characteristic of a specific VV with respect to sensitivity to establish not the frequency of the explosion, for example, with the impact in a drop hammer, but certain simpler properties of the explosive, determining its thermokinetic and physico-mechanicial properties. However, approximate characteristics of these properties can be obtained also by means of a drop hammer. A defect in the method of determining the sensitivity of VV in a drop hammer, is ~~in~~ essence the qualitative character of the results, but an advantage is the fact that the determination is made under conditions, corresponding to those under which is triggered the explosion on impact (higher, rapidly changing pressure, movement of substance et al.).

Above we mentioned that for the triggering of an explosion on impact, there are both physical, as well as chemical factors. One should, however, emphasize the difference between them. The chemical factors continuously are associated with the explosive and play their own role under all conditions; the role of the physical factors is shown only under definite, more or less specific conditions for each VV. Therefore, if we have an explosive, the sensitivity of which is small, as the result, of the chemical factors, i. e., such VV, for which are characteristic, a low inflammability and a large critical diameter of detonation, then for the triggering of its explosion a strong or dimensionally large local heat-up is necessary. This substance will be exploded only under those conditions of mechanical effects, which assure generation of such a heat-up. Conversely, an explosive, with the same physical properties, but with a high "chemical" sensitivity, will be exploded not only during these mechanical effects but also during many others, which create weaker heat-ups from which the first explosive did not explode.

The statement above by no means means that an explosive with a high "chemical" sensitivity always will give a large frequency of explosions. Conversely, there may be such conditions of mechanical effects, with which frequency of explosions of "chemically" less sensitive substance will be greater. A good example is azide of lead,— a substance with a high "chemical" sensitivity, which on impact in a drop hammer along normals owing to low fluidity is exploded with greater difficulty than, for example, tetryl, the "chemical" sensitivity of which is by far much lower. However, on an average, under the various conditions of mechanical effects which are possible in practice an explosive with high "chemical" sensitivity will be more dangerous, than a VV, which has a low sensitivity. The latter will be dangerous only during certain conditions of the effect, when the specific mechanical properties of the explosive create the possibility of generation of a sufficiently intense seats of high temperature and of a development of a burning which had started in them.

Thus, for example, according to the experiment by N. A. Kholevo, trotyl, in mixture a with an aluminum powder (80:20), on impact between two steel rollers with a diameter of 10 mm (instrument No 2) does not give explosions even with a great impact energy (4 kgm). It is difficult to force it to explode also from friction. If, however, the indicated mixture is placed in instrument No 1, where owing to narrow gaps between rollers and sleeve, the flow of substance is hampered, then the frequency of the explosions with that same impact energy amounts to 100 %.

We now cite a second example. If on the drop hammer in instrument No 4 (see below) we produce an impact by nitroglycerine or azide of lead, after having slightly raised the upper roller above the VV, then there can be obtained a frequency of explosions 100%, supposedly owing to the capture of air. With the roller, placed directly on explosive, it is equal to zero. If, however, we take chemically a relatively little-sensitive explosive (for example, tetril or hexogene) then the existence of an interval between the upper roller and the VV does not result in a marked increase in the frequency of explosions[1].

The question concerning how it is possible according to results of the test on the drop hammer to estimate "The chemical" and "mechanical" aspect of the sensitivity of a VV, is examined below in specific experimental data.

Experiments were made in instrument No 4, the scheme of which is given in Fig. 1. From the scheme of this instrument it is seen that it basically corresponds to N. A. Kholevo's instrument No 2; its chief distinction consists in the fact that, in it are used rollers of large diameter (19 mm), but the point of their junction along the entire perimeter does not touch the walls of the sleeve, so that VV during expiration, caused by the impact, is ejected into unlimited space.

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[1] See present collection of articles, page 99.

Table 1. Results of Experiments with Certain Explosives on Drop Hammer in Instrument No. 4 (Load 10 kg. height of its fall 25 cm, number of experiments in each group 25, rebound of load during non-loaded impact 70% of height of its fall)

1 Серия опытов	2 Взрывчатое вещество	3 Навеска, мг	4 Условия опыта	5 Частость взрывов, %	6 Средний отскок груза при отказах, % высоты падения
1	7 Гексоген	1 5 10 50	12 Навеска расположена кучкой в центре ролика	8 64 80 92	64 64 60 54
		10 50	13 Навеска размещена равномерно по всему торцу ролика	0 8	65 64
2	8 Тротил	5	12 Навеска расположена кучкой в центре ролика	0	61
		5	14 Навеска размещена равномерно по торцу ролика	0	65
		50	15 Таблетка диаметром 10 *мм* расположена в центре ролика	0	39
		50	12 Навеска расположена кучкой в центре ролика	0	41
		50	14 Навеска размещена равномерно по торцу ролика	4	35
3	9 Тетрил	5	16 Закристаллизовавшаяся капля	16	54
		10 20 50	12 Навеска расположена кучкой в центре ролика	4 48 12	57 57 43
		50	14 Навеска размещена равномерно по торцу ролика	24	50
4	10 Нитроглицерин	2 5 10	17 На нижний ролик наносится капля; под тяжестью веса верхнего ролика она растекается между торцами	4 8 0	61 60 61
11 5	Нитроглицерин желатинированный	2 5 10	17 На нижний ролик наносится капля; под тяжестью веса верхнего ролика она растекается между торцами	4 4 0	66 67 65
6	Нитроглицерин	10	18 В навеске находятся 2—3 стальных крупинки толщиной 0,01—0,04 *мм*	28	

1) Series of experiments; 2) Explosive; 3) Batch mg.; 4) Conditions of experiment; 5) Frequency of explosions %; 6) Average rebound of load during failures % height of fall; 7) Hexogene; 8) Trotyl; 9) Tetryl; 10) Nitroglycerine; 11) Gelatinized nitroglycerine; 12) Batch is located in small pile in center of roller; 13) Batch is distributed evenly along entire block-wood pavement of roller; 14) Batch is distributed evenly along block-wood pavement of roller; 15) Tablet with diameter 10 mm located in center of roller; 16) Crystallized drop; 17) Drop is applied to lower roller, under weight of upper roller it spreads between block-wood pavements; 18) In the batch are 2 to 3 steel grains with thickness of 0.01 to 0.04 mm.

Peculiarities of the deformation of the batch of VV and the generation of the explosion in instrument No 4, as well as its advantages and defects of its construction, will be discussed later, but now we will dwell on results of tests of certain VV in this instrument on the drop hammer. These results are presented in table 1.

In experiments with each VV under study, the amounts of the batch and its distribution on block-wood pavement of the roller varied. Besides frequencies of the explosions, also the height of rebound of load after impact (in % of height of fall) in cases of failures was fixed. The first series of experiments were made with hexogene, in which the batch of VV in a small pile was placed at the center of roller. With a little batch (1 milligram) the frequency of explosions was 8%, with 5 milligram it increased to 64%. With a subsequent increase of the batch amounts double and 10 times the orginal batch, the frequency of the explosions continued to increase. If, however, a large batch of VV were placed evenly on the block-wood pavement of the roller, then the frequency of explosions sharply falls. This points out to the fact that hexogene flows with difficulty, and that the pressure, which will be attained with the distribution of the impact energy over the entire area of the roller, to the same small thickness of the layer, is insufficient to cause a flow of the substance, and consequently, to cause an explosion. This is confirmed also by comparing the heights of a rebound of the load. With an evenly distributed layer of VV the height of the rebound is great and approximates the height observed in experiments without loads, this indicates a lack of flow in the substance; such height of rebound is observed with a central location of small batch which points out in this case the small expenditure of energy for the flow in VV. With a central location of a large batch (50 milligram) the rebound decreases markedly.

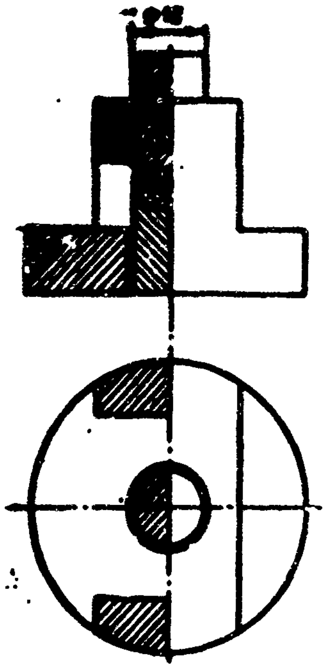

Fig. 1. Diagram of instrument No 4 in testing explosives for sensitivity on impact.

The question, however, arises by what, then, is determined the low frequency of explosions with very small centrally located batches of VV (1 milligram)? It would have been possible to assume that a significant part of energy of the impact is expended during the deformation of the charge, in the process of which the diameter and resistance to flow of VV increases. When such a thickness of the layer VV, is attained with which a continuation of flow would cause an explosion, the energy of load was exhausted so much that flow weakens or ceases. However, opposed to this explanation is the high frequency of explosions with batches of 10 and 50 milligrams in comparison to 1 milligram. One must therefore assume that with a small batch, by the moment, when resistance to the flattened tablet becomes significant, we have already entered into a region of such small thicknesses, with which the thermal losses do not permit burning to be developed.

Thus, by combining these data it may be concluded, that hexogene is characterized by high "chemical" sensitivity, because it explodes even with very small batches. In connection with the fact that this VV possessed small fluidity, its high sensitivity can be developed only in the case, when conditions of the deformation favor the generation of the flow of the charge (large specific pressure and facilitated conditions of flow -- instruments No 2 or 4 with a central placement of the batch).

Let us examine now the results of the experiments with trotyl. With a batch of 5 and 50 milligrams we do not obtain explosions by placing the VV either at the middle of the roller, or over the entire area of its block-wood pavement. This, one must explain by the fact that trotyl possesses great fluidity which is confirmed also by the magnitude of the rebound, and simultaneously it is chemically little-sensitive.

With small batches it does not explode, because thickness of layer becomes less critical. Trotyl does not explode also with large batches (large thickness of layer), because owing to the great fluidity there does not occur (with given dimensions of the roller) a stress, sufficient for a triggering of the explosion during the flow. Tetryl occupies an intermediate position. Its fluidity is higher than that of hexogene with a batch of 50 milligram, evenly distributed on the roller, it explodes with a frequency in any case of no less, than with a central location (of batch), while in the case hexogene the frequency of the explosions with an even distribution, as we have seen, sharply fell. Parallel with this a comparison between magnitudes of the rebounds shows that tetryl in distinction from hexogene flows fairly well -- the rebound (with an even distribution in a batch of 50 milligram) amounts to only 50% in distinction from 64% for hexogene. On the other hand, tetryl "chemically" is less sensitive, than hexogene: the frequency of explosions of tetryl becomes small (16%) even with a batch of 5 milligram, with which hexogene gives even 64% explosions.

The behavior of liquid VV under the described conditions of an impact can be illustrated by experiments with nitroglycerine. It gives under ordinary conditions of test a very low, or nearly zero frequency of explosions with batches from 2 to 10 milligrams. Fluidity of nitroglycerine is high; this is confirmed especially by the large magnitude of its rebound. In it there does not occur on impact, such high stresses during which the coefficient of internal friction would be increased to a degree, sufficient for the generation of critical heat-ups. Therefore, although "chemically" nitroglycerine also is very sensitive, this sensitivity under the indicated conditions cannot be developed. The behavior of nitroglycerine under these conditions is analogous to the behavior of trotyl, which although less fluid, but simultaneously also is much less sensitive chemically.

In this connection, however, arises the question: why is an explosion of nitroglycerine, and also of trotyl, much more readily triggered in instrument No 1 and how by not resorting to this instrument, it is possible to characterize the sensitivity of such explosives?

As we have already frequently mentioned, an explosion develops on impact in a drop hammer, if/ there is/ possible not only a generation of a chemical transformation of the substance, but also propagation and development of this transformation up to the explosion.

For the generation of a transformation, a fairly stressed flow is necessary, but for its propagation a sufficient thickness of layer of the substance. In instrument No 1 is realized a combination of both conditions, a stressed flow in the gap, more precisely in that portions of it where the roller, which after having been extended on impact, serves as a clearance of the gap and the thicker layer of substance in that part of the gap, where the roller was less extended, and also between the block-wood pavements, where substance did not succeed even in being extended.

In order to reproduce such conditions, favoring the generation of an explosion of VV with high fluidity, it is possible to in principle to proceed in two ways.

1. To increase dimensions (height and diameter) of the charge, but correspondingly also of the rollers, as well as weight of the load; then the

large stresses during the flow will generate with the thickness of the charge even exceeding the critical, and the generated heat-ups may develop into an explosion.

2. On the block-wood pavement of roller to make a hole and to place into it more VV, than corresponds to its volume; in this case the surplus of explosive on impact will be forced between the block-wood pavements of the rollers in the form of film analogous that, which takes place in the gpa of instrument No. 1; the generated ignition on the edge of the hole will be able to spread in the thick layer of the explosive, located in the hole; with such a setting-up of the experiment the role of the gaps of instrument No. 1 is fulfilled by gap the between block-wood pavements of rollers[1].

The results of experiments with nitroglycerine, carried out by this scheme are presented in table 2.

Table 2

Frequency of Explosions of Nitroglycerine in the Instrument, Having Roller With A Hole (Volume of hole of 0.01 cm^3, its diameter 5 mm, depth 0.8 mm; load 10 kg. height of its fall 25 cm).

1) Навеска в мг	2) Число взрывов / 3) Число опытов
10	4 5/5
14	9/10
28	4/10

1) batch in milligram; 2) number of explosions; 3) number of experiments.

Another possibility "of the manifestation" of the potential sensitivity of a flowing explosive consists in the fact that in order to artificially form in it during the impact on the drop hammer, seats of heat-ups, which the flow of VV through itself owing to the small coefficient of internal friction (viscosity) cannot create. This can be attained, for example, by introducing into the explosive a few hard

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[1] If the hole is filled only partially and nitroglycerine does not fall into the gap between block-wood pavements of the rollers then explosions are not observed; they generate also with great difficulty, if in the space between block-wood pavements during impact too much liquid is forced.

particles, the friction of which along the surface of the firing pin or anvil results in heat-ups. Experiments confirm the reality of this possibility (see series 6 in table 1).

It is possible to hamper during experiment the flow of VV by placing a readily flowing (explosive) / into/ a cup made of soft metal. In the table 3 are presented results of respective experiments with trotyl and nitroglycerine.

Table 3

Frequency of Explosions of Explosives, Placed Into a Cup Made of Red Copper. (Volume of cup 0.035 cm^3, its diameter 5 mm, height 1.8 mm; load 10 kg, height of its fall 25 cm).

1) Взрывчатое вещество	2) Навеска в мг	3) Число взрывов 4) Число опытов
5) Тротил	50	7/25
6) Нитроглицерин	30	6/10
	40	4/10
	50	3/5

1) Explosive; 2) Batch in milligram; 3) Number of explosions; 4) Number of experiments; 5) Trotyl; 6) Nitroglycerine

Thus, the cited results of the experiments agree well with ideas concerning the mechanism of the triggering of the explosion on impact, advanced and developed by N. A. Kholevo. These ideas should serve for evaluating the sensitivity of explosives to mechanical effects. They make it possible in reference to impact conditions approximately to differentiate the role of chemical and physico-mechanical factors of the sensitivity and correspondingly provide the possibility of obtaining a more complete idea about the properties of VV, than with standard method of testing.

On the Methodology of Testing Explosives for Sensitivity during Impact

At present, the testing of VV for sensitivity during impact is regulated by the All-Union Government Standard 4545--48 and 2065--43. These standards specify the placing of the explosive during test in a roller device which is a simplified variant of the Kast stamping instrument proposed by Kast in 1906.

As the basis of the mechanism of stamping instrument were assumed the following considerations which then seemed indisputable: large oscillations in the results of tests, observed with a drop hammer, are caused by the inconstancy of impact conditions, in particular of the area of the charge, on which the impact operates and by the unparallelism of the surfaces being impacted. In the respect, friction is added to the impact effect. For the removal of these presumed defects, (first) a Kast design, but later a contemporary design of an instrument for testing VV on a drop-hammer was adopted.

In the last decade, however, it has been shown, chiefly by works of N. A. Kholevo, that with an impact on a drop hammer the explosion in many cases generates, apparently, not between the block-wood pavements of rollers, but during the punching of the VV under the effect of the impact into the gap between rollers and the directing sleeve. In accordance with this even if during the testing a constancy of the area of impact and direction of movement of the impacted surfaces, had been assured but conditions of the flow of VV after its exit from the space between block-wood pavements of rollers were varying, then the frequency of explosions can vary sharply. The role of these conditions graphically is demonstrated by results of tests in N. A. Kholevo's instrument No 2[1]. Tests in instruments of two types-- with hampered (No 1) and facilitated (No 2) flow of the charge gives a more complete idea about the sensitivity of VV, than a testing in one of them. The specified All-Union Government Standard 2065 -- 43 instrument, in which rollers have bevel edges, occupies an intermediate position between instruments No 1 and 2.

However, if an explosion occurs in the gap between the rollers and sleeve and its initiation depends on the magnitude of this gap, then the design of such an instrument cannot be considered rational. In reality the magnitude of gap can irregularly change from experiment to experiment owing to the

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[1] See article N. A. Kholevo in present collection of articles (page 5).

displacement of axis of rollers with respect to the axis of the sleeve channel. During the impact a pressing of VV into the gap usually occurs, as it was possible to see in experiments where the VV flowed beyond the channels, one-sided, obviously where the gap was wider. Furthermore, the sleeve channel ideally should fulfill only the function of directing the movement of the roller and therefore for corresponding dimensions (internal diameter) and for manufacturing its surfaces there are high requirements. Inasmuch as actually it serves as place where the explosion generates, then the gases of explosion rapidly erode the channel and make it little useful for an accurate directing of the movement of the roller. To a known degree this refers also to instrument No 2; although the explosion in it occurs not in the gap, nevertheless gases can leave only through the sleeve channel and therefore they also cause its erosion.

In the light of these considerations it appeared expedient to change the design of the instrument in order that hot gases in the explosion did not enter into the channel of the directing sleeve and did not cause its fast wear. This also was realized in instrument No 4, in which the sleeve can serve without replacement for a long time. Besides increasing the constancy of testing conditions this change of construction in the instrument lowers the cost of the test. A sleeve of required All-Union Government Standard quality (as distinguished from rollers) is fairly expensive, but during testings with instruments No 1 and 2 of thick VV, the deformation and erosion of the channel proceeds rapidly and the sleeve must frequently be changed. Certain investigators were limited even to only a single use of the sleeve which very much increased cost of the test.

The use of instrument No 4 considerably reduced the cost and would allow one instrument to obtain that characteristic of sensitivity, which up to now could be obtained only by testing the VV in two instruments — No 1 and 2.

The main advantage of a complex test in instruments No 1 and 2 consists in that it makes it possible to characterize not only thermokinetic, but also the physico-mechanical aspect (in particular fluidity) of the sensitivity of VV. Both these characteristics, as we have seen, can be established in the proposed instrument No 4 in following the methodology of testing hard explosives: the VV are tested with two locations of the batch on the block-wood pavement of the lower roller.

1) in the form of slightly (from the hand) depressed tablet with a diameter 5 mm, placed in center of the roller (such a location in the future for brevity will be called central);

2) in the form of layer of even thickness, distributed over entire block-wood pavement of roller (in the future will call "uniform spreading").

The tests are made with batches of several magnitudes [1] and besides for every batch and every variant of its distribution on the roller, a definite number (for example, 25) parallel experiments, establishing frequency of explosions, are made in the experiments, where there was no explosion, the height of rebound of load after impact is fixed.

With a central location are created facilitated conditions of flow of VV, analogous to those realized in instrument No 2, where there is combined, the small diameter of rollers (large pressure on impact) and presence of a groove. In the case of central location of the batch (in instrument No 4) the flow is facilitated by a concentration of the impact energy in a small area of the charge and by relatively large gaps between the rollers. An even distribution of the charge creates hampered conditions for the flow of VV, because the

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[1] Judging from the obtained experimental data, a sufficiently complete idea on the sensitivity of ordinary VVs can be obtained with the testing of two batches, 10 and 50 milligrams

impact effect in this case is apportioned to a large area and the pressure is small, but the gap between rollers in the initial stage of the impact is smaller than with a central location of the batch.

We consider now the interpretation of possible results of experiments with various VV.

Let us assume that with an even distribution of a small batch a low frequency of explosions is obtained. This can occur for two reasons:

1) substance thermokinetically is little sensitive and does not explode in a film;

2) its fluidity is small and it does not flow under given conditions.

We repeat the experiment with a central location of the batch, which assures greater pressure during impact and facilitates the flow of VV. If the frequency of the explosions increases, then a lack of them or smaller frequency with an even distribution were the result of a small fluidity. As an example of such substances (table 4) the following may serve: hexogene, octogene, T. E. N. trinitro resorcinate of lead et al.

If, however, for two VV with a small batch there is obtained a small frequency of explosions both with an even distribution as well as with a central location, then this still does not mean that they have an identical low sensitivity. The small frequency of explosions may be caused by the fact that for both substances with small batch of a too fine layer of VV, thinner, than it is necessary for the propagation of the burning or the explosion. The distinction between the substances then will be developed with large batches. The little-sensitive substance as before will not give explosions; substance with the greater sensitivity will begin to give them with a greater frequency. As an example it is possible to point to trinitroaniline and styphnate of potassium. Both they in small batches do not explode; however trinitroaniline does not explode also with a change in large batches, while styphnate of potassium (with a central location) gives 100% explosions.

A test with an increased batch (50 milligram) is useful and in this respect it makes it possible according to amount of rebound of load during failures to judge about the fluidity of the substance.[1]

If the fluidity is small, then the VV does not succeed in being greatly extruded. The expenditure of energy in extruding it is small and therefore the rebound is large. The rebound also with a central location of the charge is large, although as a rule, it is naturally smaller than with an even distribution of VV.

On the other hand, the decrease in rebound in comparison with an unloaded impact provides the possibility of being convinced that the flow of the substance during impact takes place and that if in this respect failures are obtained, then the cause of them is not in the lack of a flow.

One should, however, point out that a large rebound can be obtained not only with the small fluidity of an evenly distributed substance, but also in the case, if the fluidity is relatively great and expenditure of energy in extruding the substance correspondingly is small. This is observed, in particular, for certain fusible VVs, for example, for trotyl. It is characteristic that in this case with central location of the batch a larger rebound, is obtained apparently, due to the melting of the substance during intense flow and the associated sharp increase in its fluidity.

The comparison of the rebound and frequency of explosions with different batches and locations of them makes it possible in most cases more fully to characterize "chemical" and "mechanical" aspect of the sensitivity of the

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[1] With small batches, the differences in rebounds during the test of the various VV are small, because the expenditure of energy in extruding the substance is relatively small.

tested VV, than by means of these indices individually.

We shall explain this by an analysis of the data in table 4, where there are reduced the results of the test by the proposed methodology 28 secondary and initiating VVs.

Trinitrobenzene has significant fluidity, about which it is possible to judge by the large decrease of rebound not only with a central, but also with an even distribution of the charge (batch 50 milligram). Simultaneously it is chemically little sensitive, and in order that explosions generated stressed conditions of flow of VV, which are created with a batch of 10 milligram and its even distribution are necessary. With a central location of the charge the flow is facilitated by the large specific pressure, and also owing to the fusion of VV during the flow, as a result the stress of the flow becomes less (in this respect it must be taken into consideration that the temperature of fusion of trinitrobenzene with respect to temperature of the flash is low).

Trotyl is chemically close to trinitrobenzene, but its fluidity is significantly greater. With a central location of the trotyl charge the rebound is considerably greater than in the case of trinitrobenzene. Fluidity of trotyl is so great that a decrease in the batch to 10 milligram results in a significantly smaller (to 24% instead of 56% for trinitrobenzene) increase in the frequency of explosions even with an even distribution of the charge. A subsequent decrease of the batch of trotyl (to 2 milligram) does not give an increase in the frequency of explosions. Apparently, the thickness of layer of VV is found to be in this respect less critical for burning. The combination of the chemical inertness and the significant fluidity also makes trotyl one of the least sensitive explosives, being practically applied.

Picric acid will behave analogously to trinitrobenzene. Its fluidity is markedly less (rebound larger), but its chemical sensitivity is greater.

The maximum of the frequency of explosions of picric acid occurs as well as with trinitrobenzene with a batch of 10 milligram and with its even distribution. The distinction from trinitrobenzene consists in the fact that in picric acid is observed a significant frequency of explosions also with a central location of the charge.

With trinitroresorcin the fluidity is even less, and with a uniform distribution it shows a low frequency of explosions with all batches. Chemically it is more sensitive than picric acid and it gives high frequency with a central location of the charge even with the smallest batch.

Physically similar to trinitroresorcin is trinitroxylene, but chemically it is less sensitive and the maximum of frequency of explosions with it is lower.

Nitroamine (trinitroaniline and trinitrodiaminobenzene) are characterized by a low fluidity. With an even distribution of 50 milligram the rebound corresponds to an unloaded impact and a frequency of explosions equal to zero. However, frequency of explosions remains low and with a central location of the batch, when judging by the rebound the flow of VV takes place. This attests to the fact that also the chemical sensitivity of nitroamine is small which first was marked by F. A. Baum.

Tetryl according to fluidity is close to picric acid, it is close to it also with respect to frequency of explosions under various conditions.

Table 4

Results of test of explosives on a dro- hammer in instrument No. 4. (Load 10 kg. height of its fall 25 cm. number of experiments in each group 2 , rebound of load with unloaded impact below 72% of the height of it fall).

Conventional designations: 70 - central location; 80 - uniform distribution.

1) № по пор.	2) Наименование вещества	3) Температура плавления °C	4) Расположение навески ВВ	5) Величина навески ВВ 6) 2 мг 7) % взрывов	8) Средний отскок груза при отказах в % высоты падения	10 мг 7) % взрывов	8) Средний отскок груза при отказах в % высоты падения	20 мг 7) % взрывов	9) Средний отскок груза при отк. [illegible] и отклонения его от среднего значения в % высоты падения
1	10) Тринитробензол	122,5	70 Ц	4	70	8	66	4	38^{+22}_{-14}
			80 Р	20	68	56	66	4	$42^{+[illegible]}_{-14}$
2	11) Тринитротолуол	80,5	70 Ц	0	68	0	66	0	47^{+4}_{-5}
			80 Р	4	68	24	67	4	42^{+12}_{-16}
3	12) Пикриновая кислота	122,5	70 Ц	12	69	32	68	36	47^{+9}_{-7}
			80 Р	0	69	64	69	24	56^{+9}_{-17}
4	13) Тринитрорезорцин	178	70 Ц	32	70	32	62	84	40^{+34}_{-34}
			80 Р	4	71	0	71	8	68 ± 5
5	14) Тринитроксилол	182	70 Ц	8	71	20	64	44	48^{+12}_{-18}
			80 Р	4	70	12	66	36	62^{+4}_{-3}
6	15) Тринитроанилин	191.8	70 Ц	0	72	4	62	12	48 ± 30
			80 Р	0	72	0	71	0	70^{+3}_{-13}

1) Number chronologically; 2) Name of explosive; 3) Temperature of melting C; 4) Location of batch of VV; 5) Size of VV batch; 6) milligram; 7) % explosions; 8) Average rebound of load during failures in % of fall; 9) Average rebound of load during failures and its deflection from the mean value in % height of fall; 10) Trinitrobenzene; 11) Trinitrotoluene: 12) Picric acid; 13) Trinitroresorcin; 14) Trinitroxylene; 15) Trinitroaniline

Table 4 (continued)

7	16 Тринитродиаминобензол	289	70 Ц	4	70	32	66	4	45^{+7}_{-6}
			80 Р	0	70	0	65	0	68±0
8	17 Тетрил	129	Ц	16	72	20	66	16	45^{+12}_{-14}
			Р	8	72	0	66	44	52^{+19}_{-14}
9	18 Гексил	240	Ц	96	68	100	—	92	52±0
			Р	8	69	8	63	8	65^{+7}_{-5}
10	19 Гексоген	204	Ц	96	72	92	65	92	54±1
			Р	0	72	0	68	0	66^{+3}_{-4}
11	20 Октоген	280	Ц	92	72	100	—	—	—
			Р	0	72	0	71	4	68±3
12	21 Тэн	140	Ц	64	71	92	64	84	52^{+5}_{-13}
			Р	0	70	0	67	8	68^{+2}_{-3}
13	22 Дина	52	Ц	16	72	44	65	60	61±3
			Р	4	72	68	68	88	61^{+4}_{-2}
14	23 Гексанитродифенил	240	Ц	28	70	68	62	44	48^{+5}_{-9}
			Р	0	72	0	71	28	66^{+3}_{-7}
15	24 Гексанитродифенилоксид	260	Ц	92	72	100	—	60	50±4
			Р	84	72	68	70	20	57^{+4}_{-5}
16	25 Гексанитрооксанилид	331	Ц	76	71	100	—	100	—
			Р	0	72	4	70	8	67^{+4}_{-1}
17	26 Пикрат лития	—	Ц	20	69	12	66	16	42^{+28}_{-16}
			Р	0	71	0	67	12	70^{+3}_{-4}

16) Trinitrodiaminobenzene; 17) Tetryl; 18) Hexyl; 19) Hexogene; 20) Octogene; 21) T. E. N. ; 22) Dyne; 23) Hexanitrodiphenyl; 24) Hexanitrodiphenylksid; 25) Hexanitrooxanilide; 26) Picrate of lithium.

Table 4 (continued)

1 № по пор.	2 Наименование вещества	3 Температура плавления °C	4 Расположение навески ВВ	5 Величина навески ВВ					
				6 2 мг		10 мг		50 мг	
				7 % взрывов	8 Средний отскок груза при отказах в % высоты падения	7 % взрывов	8 Средний отскок груза при отказах в % высоты падения	7 % взрывов	9 Средний отскок груза при отказах и отклонение его от среднего значения в % высоты падения
18	10 Пикрат свинца	—	Ц	—	—	100	—	—	—
			Р	—	—	88	64	—	—
19	11 Пикрат калия	—	Ц	68	72	100	—	96	54
			Р	0	68	0	68	8	65^{+4}_{-10}
20	12 Стифнат калия (двузамещенный)	—	Ц	4	72	100	—	100	—
			Р	0	72	0	70	0	68 ± 3
21	13 Азид аммония	—	Ц	8	69	64	60	0	36^{+28}_{-28}
			Р	0	72	4	70	4	55^{+13}_{-18}
22	14 Азид свинца	—	Ц	100	—	—	—	—	—
			Р	8*	64	—	—	—	—
23	15 Азид кальция	—	Ц	100	—	—	—	—	—
			Р	12*	64	—	—	—	—
24	16 Гремучая ртуть	—	Ц	100	—	100	—	100	—
			Р	60	72	92	68	96	70
25	17 Тринитрорезорцинат свинца	—	Ц	100	—	100	—	100	—
			Р	0	71	56	71	12	68^{+5}_{-3}
26	18 Тетразен	—	Ц	100	—	100	—	—	—
			Р	20	68	64	71	96	72
27	19 Черный порох	—	Ц	64	68	84	80	96	50
			Р	8	70	16	68	0	68^{+2}_{-1}
28	20 Перхлорат аммония	—	Ц	48	70	84	59	84	57^{+7}_{-2}
			Р	—	—	4	72	0	72 ± 3

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21 * Навеска 20 мг.

1) Number chronologically; 2) Name of explosive; 3) Temperature of melting C; 4) Location of batch of VV; 5) Size of batch of VV; 6) milligram; 7) % explosions; 8) Average rebound of load during failure in % height of fall; 9) Average rebound of load during failure and its deflection from mean value in % height of fall; 10) Picrate of lead; 11) Picrate of potassium; 12) Styphnate of potassium (direplaced); 13) Ammonium azide; 14) Lead azide; 15) Calcium azide; 16) Mercury fulminate; 17) Trinitroresorcinate of lead; 18) Tetrazene; 19) Black powder; 20) Perchlorate of ammonium; 21)*Batch at 20 milligrams.

Heterocyclic N-nitramines (hexogen and octogen) have a low fluidity, but are chemically sensitive and with a very high frequency explode with a central location of the batch.

Hexyl and T. E. N. exhibit a low fluidity and correspondingly significantly higher frequency of explosions with a central location of the charge in comparison with an evenly distributed charge.

Hexanitrodiphenyl has a relatively low fluidity, therefore as distinguished from trinitrobenzene in batches of 2 and 10 milligram with an even distribution, explosions are not obtained. They are observed with moderate frequency with a batch of 50 milligrams. With a central location of the charge the frequency of the explosions of hexanitrodiphenyl as distinguished from trinitrobenzene is significantly more. An analogous picture is given by hexanitrooxanilide, but it has a greater frequency of explosions with a central location of charge than hexanitrodiphenyl has.

Picrates and styphnates of potassium and lithium exhibit a low fluidity and correspondingly small frequency of explosions with an even distribution of the charge; with a central location the frequency of explosions by them is high with the exception of picrate of lithium which, possibly is associated with its greater hygroscopicity.

Azides (of ammonium, lead and potassium) are characterized by a low fluidity and a correspondingly small frequency with a uniform distribution of the batch, but due to high chemical sensitivity the frequency of explosions with a central location of these VV charges becomes high.

To the poorly flowing explosives belong black powder and perchlorate of ammonium; with a central location they give a high frequency of explosions.

The behavior of certain of the studied explosives is very unusual. As, tetrazene and mercury fulminate flow poorly, but nonetheless they exploded with great frequency; hexanitrodiphenyloxide and dyne do not differ essentially with respect to rebounds with a central location and even distribution of the charge; they do not exhibit a special difference also in the frequency of explosions.

In the case of testing initiating VVs with a high chemical sensitivity for the generation of the burning and explosion the small local **displacements**, which precede macroflow, **possibly** are sufficient. The modificational transitions with a higher pressure, may play the role for a dyne.

On the whole, tests by the given method makes it possible by means of one instrument to obtain much more comprehensive evaluation of the sensitivity of hard VV to impact, than is provided by the standard method. By varying during the experiment flow conditions of the VV by means of changing the location and magnitude of the batch and by registering the frequency of explosions and the magnitude of rebound (during failures), it is possible to give an evaluation of an explosive with respect to the danger of the generation of an explosion under different conditions. This evaluation is not expressed in absolute units. Such an expression has no meaning, inasmuch as, as we have seen, the frequency of the explosions of one and the same with a given energy of the effect may vary within wide limits. The chief factors of this frequency of the properties of explosive are inflammability and fluidity. As is clear from the above-mentioned statement, also conditions of the mechanical effect may be the decisive effect. Therefore an evaluation of the sensitivity of VV irrespective to conditions of this effect are devoid of practical meaning.

In the described experiments above we used a 10 kg load and applied only one height of fall 25 cm only because these conditions are the most commonly used. It is natural that various heights and loads can be used. In exactly the same way it is possible to determine not only frequency under given conditions of the impact, but also the lower limit of conditions, starting from the one explosions are obtained.

One should dwell on the question of testing liquid explosives. Their fluidity is too great with a given diameter of rollers and rate of impact as a result of the flow to produce heat-ups, sufficient for the generating of an explosion. A stressed flow generates in instrument No 4 only with such a thin layer that no longer is capable of being exploded. Therefore, even if the capability for propagation of the explosion in the given liquid VV is relatively great, as takes place in case of nitroglycerine the frequency of explosions in it results in being close to zero. Ascertaining the sensitivity of nitroglycerine, and it is high, is possible only in case, the generation of a heat-up in it during impact is assured by certain special procedures. It is possible, for example, for this purpose to introduce into the nitroglycerine hard particles, to make a hole on the block-wood pavement of the roller or to place the liquid in a cup of relatively soft metal. Finally, it is possible to assure the generation of an explosion of nitroglycerine by means of a gas bubble , by placing a batch of VV on an anvil in the form of ring, as did Bouden, or by realizing an impact with the upper rollers raised somewhat.[1] The real great danger of liquid nitroglycerine in technology is caused, apparently, by just the two latter impact conditions.

The statement on liquid VVs pertains also to such hard, but very fluid and simultaneously chemically little sensitive explosives, as trotyl. For it, even those the most stressed flow conditions, which are created with a uniform distribution of the charge, do not result, as a rule, in an explosion - with small batches, because the explosion cannot be propogated in such a thin layer, with larger batches because it does not generate. Again also in this case in order to obtain an explosion, it is necessary to combine conditions of requisite

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[1] See present collection of articles, page 99.

for the generation and propagation of an explosive transformation. This was observed in instrument No 1 with a definite size of the gap, but in instruments No 4 and 2 -- within the narrow interval of conditions of the experiment (see for example, table 4), with the introduction of grains steel into trotyl, and also with the roller with a hole. Probably the explosion of this VV can be obtained with great frequency and under ordinary conditions of tests on a drop hammer, after increasing the scale of the experiment in order to realize a stressed flow with a greater thickness of the charge. Such conditions in technology however, are rarely encountered by which a very small sensitivity of trotyl under practical conditions of its use is stipulated.

In conclusion, one must point out that although the described method of the test gives the best idea on sensitivity, by which the standard is the simpler and cheaper in execution, but still the bias in principle of the test for sensitivity during impact as characteristics of the danger of explosive in handling, is maintained also in it. This bias consists first of all in that the test on the drop hammer characterizes chiefly the possibility of the generating of seats of an explosion, but does not give a true idea on the possibility of its propagation. Besides, even the possibility of the generation of an explosion during an ordinary impact along a normal is limited by fluidity of substance, because, for example, azide of lead in this case may produce a lower frequency of explosions, than trotyl. This last defect can be removed during the test by applying a slipping impact. For removal of first defect, there is necessary a test on the drop hammer to supplement the determination of the capability of VV for the propagation of burning or explosion under those conditions, necessary to determine the danger in handling with a given explosive. Only such a supplement will make it possible to establish that for example, perchlorate of ammonium, on the basis of frequency of explosions is close to T. E. N and black powder, it is incomparably less dangerous, than T. E. N., inasmuch as the critical diameter for the detonation of T. E. N. is only a tenth of that for perchlorate. Perchlorate of ammonium also is by far much less dangerous, than black powder, because the critical diameter for burning of black powder under atmospheric pressure is about 1 mm, but for perchlorate of ammonium about 33 mm. The very low critical diameters for burning even at atmospheric pressure and for detonation characterizing the initiating explosives are the main cause of their great danger in handling. Inview of these considerations, one must assume that in the future, the determination of the capability for burning and detonation in combination with test for a slipping impact will become the chief method of the characteristic of danger VV in handling.

Conclusion

A complex method of determining the relative sensitivity of VV to mechanical effects is proposed. An explosive is subjected to impact between block-wood pavements of two rollers of significant diameter, in which the space, surrounding the joint of rollers is open; the size of the batch its location on block-wood pavement of rollers vary. Advantages of this method in comparison with the standard is the great possibility of differentiating the chemical and physical factors of the sensitivity and rational design of the instrument, which considerably increases its life and constancy of test conditions and lowering their cost.

MT-63-254 Chapter 1 Article 5

Pages 72—80

K. K. Andreyev and Yu. A. Terebilina

5. Concerning the Question of the Influence of Air Inclusions On the Appearance of Explosion Under Impact

The majority of investigators considers well-grounded that the chemical reaction and explosion under impact appear not from mechanical action as such, but as a result of heatup caused by the latter. In the question about in what ways heatups actually appear in different explosives and at various conditions of impact, however, there is no full clarity.

Two main points of view received the biggest development lately. N. A. Kholevo [2] as the main way of excitation of the reaction at impact considers the flow of the explosive and its local heatups, appearing due to internal friction. Bouden [3] claims that a large role is played by inclusions of gases or vapors compressible under impact, especially in the case of liquid explosives. Numerous experiments of this investigator and his collaborators [1] showed that the energy of impact, necessary for excitation of explosion of liquid explosives, can very greatly (to several orders) be decreased at introduction of gas bubbles into the explosive.

These observations were in the works of Bouden naturally explained by the fact that in gases during their adiabatic compression up to a certain definite pressure a much larger temperature is developed, than in liquids; the heated bubble of gas heats up and ignites the explosive surrounding it.

However, being correct, this explanation, apparently, does not exhaust of the roles of the bubbles. Not only high temperature,is essential , appearing at their compression, but also the conditions of interaction, in particular heat exchange, and the heated-up gas with the explosive adjacent to it. Described lower are experiments which explain what has been said.

The initial purpose of these experiments was the comparison of sensitivity of certain explosives in liquid and solid state. The experiments were conducted in instrument No.4[1]. In order to ensure identical conditions and in particular to prevent pressing of part of the substance at the conventional setup of the experiment with a liquid in a roller instrument, when the upper roller by its own weight presses the liquid, the test explosive was placed on the end of the lower roller in the form of a drop, liquid or frozen, and the upper roller was secured with the help of a rubber ring or weak spring at a small height (~3 mm) above the lower roller. Such experiments, conducted with nitroglycerine, gave an unexpectedly high frequency of explosions at the same load and height of fall, with which in usual test conditions (upper roller before impacts is on the explosive) the frequency of explosions was close to zero. Besides, it was fixed that an increase or significant decrease of quantity of liquid explosive lowers the frequency of explosions.

Thus it turned out that in a given case the results of the test are especially sensitive to the conditions of the experiment.

The effect of a lifted roller is not observed for all liquids. Thus a supercooled solution of trotyl in tetryl (50:50) or liquid dyne do not show it at least under the set conditions of the experiment.

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[1] See this collection, pages 56-58 (original text).

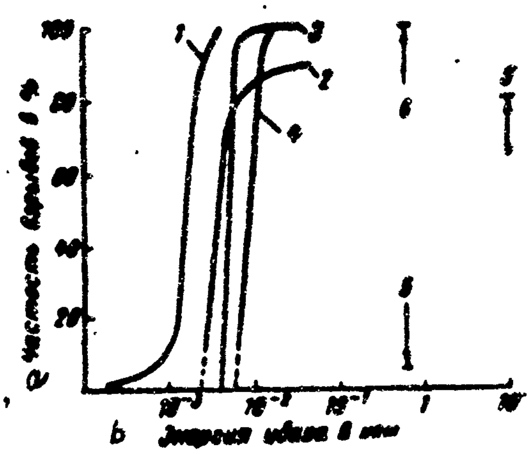

Fig. 1. Influence of conditions of the experiment on magnitude of energy of impact, necessary for excitation of a nitroglycerine explosion(according to Bouden).

1) in the striker is a hole with a little gas bubble, 2) in a layer of the explosive on the anvil are air bubbles, 3) explosive located on anvil in parallel strips, 4) explosive located on anvil in the form of separate drops, 5) impact is produced by flat striker on a film of explosive, not containing gas bubbles, 6) the same on a film of explosive, containing gas bubbles.

a) Frequency of Explosions in %; b) Energy of impact in kgm.

Analogous observations, apparently, were made also in works of Bouden with collaborators, which explained the increase of sensitivity of an explosive to impact by capture of air to the falling load. Inasmuch as the action of air is more regularily and greatly developed in the presence of deepening in the striker or with nonuniform location of the explosive liquid on the anvil, Bouden allotted main attention to these last conditions of the experiments. He notes, however, [1], that with a flat striker, falling on an open layer of nitroglycerine, a large value has the diameter of the striker, with the increase of which the frequency of explosions increases; at a diameter of a brass striker 0.6 cm, the explosion comes about very difficultly, and with a striker 2.5 cm in diameter it is much easier, which naturally explains the large probability of capture of air. Bouden indicates also that very thick layers of liquid are less sensitive, than thin ones, supposedly , because in the first case the bubble is more mobile and can escape before the pressure is increased to a significant magnitude. A decrease of frequency of explosions is observed also with too thin films.

At corresponding conditions, the entry in action of "the bubble" mechanism, the appearance of an explosion can lead to a huge increase of sensitivity of the explosive more accurately, to a decrease of the work of the impact, leading to the appearance of an explosion. The presentation about this influence is taken from the work of Bouden Fig. 1, showing the frequency of explosions of nitroglycerine depending upon energy of impact at different conditions of the experiment.

Bouden explains the observations made by him, especially in experiments with deepening in the striker, adiabatic heatup of air leading to ignition of the explosive. The principal possibility of such a mechanism of explosive ignition is indisputable. In several works, for example [4], it was shown that if the explosive were placed in a cylinder with gas and then this gas was compressed with the help of a piston impact, then the explosive is ignited. In this setup of the experiment, the mechanism of ignition, offered by Bouden, is real. However upon impact on the surface of the explosive by a freely falling striker, the process of ignition, apparently, proceeds somewhat complexly. The air between the striker and anvil, by measure of their approach is compressed and is set into motion in a radial direction with an ever increasing speed; during compression it heats up. Increased temperature is one of the main factors, determining the possibility of ignition of the explosive. The second factor —increase of pressure, which, as it is known, increases inflammability of the explosive. The third factor —movement of gas along the surface of the charge; this movement increases the heat-transfer coefficient. At last, the gas, moving along the surface of the charge at a sufficient speed of motion, can seize a drop or particle of the explosive. If this capture is not too small (then its influence is small), and not too great (then the admission of an excessively large quantity of the cold substance can lower the temperature of the heated up air), then it can greatly increase the quantity of heat, emanating at compression, and lead to ignition of the main mass of the explosive.

In Table 1 are experimental data about the influence of elevation of the upper roller of instrument No. 4 on the frequency of explosions of certain explosive in drop hammer tests. For illustration of the peculiarities of location of the explosive charge in 23--26 series of these experiments in Fig. 2 is given the corresponding diagram.

Let us consider the data of Table 1 in light of the above-expressed considerations about the mechanism of ignition of an explosive by air, heated up upon impact.

Both for nitroglycerine, and also for nitroglycol the frequency of explosions with an elevated roller is much greater than with a roller, placed on the liquid. The numbers in Table 1, when they are close to zero or to 100%, naturally, incompletely characterize the phenomenon, but the sharp difference between results at various positions of the roller is indubitable. For both explosives is observed a certain optimum magnitude of weight, the increase or decrease of which decreases the frequency of explosions. For gelatinized nitroglycerine (series of experiments 14--18) the effect of the elevated roller is completely preserved [1].

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[1] This circumstance was somewhat unexpected. Gelatinized nitroglycerine contained, as usual, many air bubbles and was not specially processed for their removal. Nonetheless with an elevated roller the frequency of explosions sharply increased. This confirms the fact that a bubble, formed on the surface, is much more effective in the sense of excitation of an explosion, than that in the mass of the substance. In this connection one should turn attention to the following circumstance. If the explosive beforehand is covered by a roller or foil, then adhesional contact between them is established. Upon impact by elevated roller the explosive arrives in contact with the surface of the metal so fast that adhesional contact cannot be established.

Table 1

Influence of elevation of the upper roller above the lower one on the frequency of explosions in tests of certain liquid and solid explosives on a drop hammer

(instrument No 4, weight of load 10 kg, height of fall 25 cm, number of experiments in series 25)

№ серии опытов (1)	Взрывчатое вещество и его расположение на ролике прибора (2)	Навеска ВВ (3) мг	Частость взрывов в % при ролике (4)		(7) Примечание
			поднятом (5)	опущенном (6)	
1	(8) Нитроглицерин в виде капли	0,25	76	—	
2		0,5	84	0	
3		5	100	8	
4		10	92	0	
5		20	80	—	
6		50	20	—	
7		10	—	40	(11) В ВВ положены 2—3 крупинки стали
8	(9) Нитрогликоль в виде капли	0,3	56	—	
9		0,5	72	8	
10		1	92	—	
11		2	72	16	
12		7,5	76	4	
13		15	28	0	
14	(10) Нитроглицерин желатинированный (3%), расположен комочком в центре ролика	2	100	4	
15		5	100	4	
16		10	80	0	
17		25	56	—	
18	(10) Нитроглицерин желатинированный (7%), расположен комочком в центре ролика	5	96	4	
19	(10) Нитроглицерин желатинированный (10%), расположен комочком в центре ролика	20	—	12	(12) Лунка в навеске
20		20	—	60	
21		50	—	15	(12) Лунка в навеске
22		50	—	65	

1) No. of series of experiments; 2) Explosive and its location on roller of instrument; 3) Weight of explosive, milligrams; 4) Frequency of explosions in % with roller; 5) Elevated; 6) lowered; 7) Note; 8) Nitroglycerine in the form of a drop; 9) Nitroglycol in the form of a drop; 10) Nitroglycerine, gelatinized , located as a lump in the center of the roller; 11) In explosive are placed 2—3 grains of steel; 12) Hole in weight.

Continuation Table 1

(1) № серии опытов	(2) Взрывчатое вещество и его расположение на ролике прибора	(3) Навеска ВВ мг	(4) Частость взрывов в % при ролике		(7) Примечание
			(5) поднятом	(6) опущенном	
23	(8) Нитроглицерин желатинированный (7%), расположен равномерно по всему ролику; между ВВ и верхним роликом фольга	5	48	—	(17) Фиг. 2a
24		5	96	—	(17) Фиг. 2b
25	(9) То же, но навеска расположена комочком в центре ролика; между ВВ и верхним роликом фольга	5	60	—	(17) Фиг. 2c
26		5	100	—	(17) Фиг. 2d
27	(10) Дина (закристаллизовавшаяся капля)	5	8	20	
28	(11) Тетрил (закристаллизовавшаяся капля)	5	12	16	
29	(12) Гексоген, расположен в виде кучки в центре ролика	20	2/15 *	0/15 *	
30	(13) Сплав тротила с тетрилом 50:50 (переохлажденная капля)	40	0	4	
31	(14) Нитроглицерин (замерзшая капля)	5	48	4	(18) ВВ покрыто фольгой
32		5	28	4	
33	(15) Азид свинца, расположен в виде кучки в центре ролика	20	100	4 **	
34	(16) Азид кальция, расположен в виде кучки, в центре ролика	20	76	12	

* In denominator—number of experiments, in numerator—number of explosives

** At lowering of roller on a small pile of explosive (d≈5 mm) it is crushed: powder is distributed on a large area (d = 10 mm). If azides of calcium and lead are applied not to a loose small pile, but in the form of tablets pressed by hand 5 mm in diameter, then with a lowered roller 100% of the explosions occur; with that same weight (20 milligrams) and large diameter of the tablet (10 mm) the frequency of explosions falls.

1) No. series of experiments; 2) Explosive and its location on roller of instrument; 3) Weight of explosive in milligrams; 4) Frequency of explosions in % with roller; 5) elevated; 6) lowered; 7) Note; 8) Nitroglycerine, gelatinized (7%), located evenly all along the roller; between explosive and upper roller of foil; 9) The same, but weight is located as a lump in the center of the roller; between explosive and upper roller of foil; 10) Dyne (crystallized drop); 11) Tetryl (crystallized drop); 12) Hexogene, located in the form of a small pile in center of roller; 13) Alloy of trotyl with tetryl 50:50 (supercooled drop); 14) Nitroglycerine (frozen drop); 15) Lead azide, located in the form of a small pile in center of roller; 16) Calcium azide, located in the form of a small pile, in center of roller; 17) Fig.; 18) Explosive covered by foil.

Frequency of explosions increases and with a lowered roller, if a small hole is made on the surface of the charge (series of experiments 19—22). Distinction in frequency of explosions with elevated and lowered roller was observed for frozen nitroglycerine, but in this case it is less.

The effect of the elevated roller is developed also in that case, if impact by nitroglycerine is accomplished through a circle of tin foil (thickness 0.05 mm)[1]. Here, if the foil is secured to the upper roller (Fig. 2b and 2d), then the frequency of explosions is obtained 100%, as without the foil. If however it is placed on nitroglycerine (Fig. 2a and 2c), then the frequency of explosions is nearly 50%.

For other studied solid secondary explosives (dyne, tetryl, hexogene) the influence of the position of the roller does not show. It is possible that this is connected with the relatively small diameter of the rollers, since capture and compression of air undoubtedly depends on this diameter.

Otherwise there is the matter with a solid initiating explosive—lead azide and calcium azide.

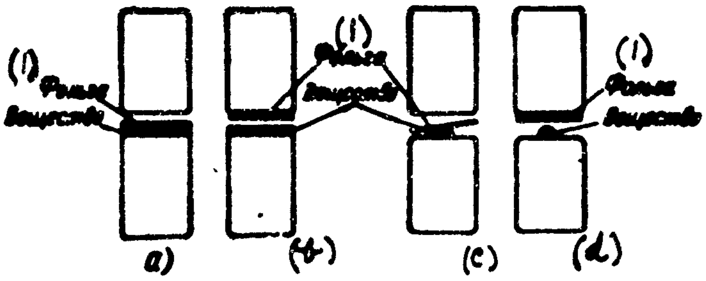

Fig. 2. Diagram of location of explosive charge and foil in certain experiments of Table 1.
a—even location of substance, covered by foil, b—foil is soldered to upper roller, c—weight is located in center of roller and covered by foil, d—foil is soldered to upper roller.
1) Foil; Substance.

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[1] In these conditions the high sensitivity of the explosive is not lowered and while on the surface of the striker instead of steel there is layer of tin, the temperature of melting of which (232°) is much lower than the minimum temperature, necessary according to Bouden for explosion a impact (400°).

With an elevated roller the frequency of explosions of lead azide constitutes 100%, with a roller, standing on the explosive,—4%. This circumstance is interesting already because for solid nonmelting substances, which both these azides are, it is difficult to present that mechanism of capture and compression of gas bubble, that Bouden takes for liquids.

Experiments with azides allowed to make observations, casting same light on the cause of the considered effect. When an explosion occurs with an elevated roller, then the trace from the explosion to the ends of the rollers by diameter is significantly greater than the diameter of the tablet; with a lowered roller the diameter of the imprint is the same as the original tablet. This confirms the fact that upon impact with an elevated roller before the appearance of an explosion the charge was expanded in a radial direction, apparently, as a result of entrainment of azide by air, displaced from the space between rollers.

Experiments with inert powder(chalk) showed that the tablet[1] upon impact on it by an elevated roller is scattered all along the end. When impact is produced on a roller, lowered on the tablet, it is crushed, but is not scattered.

The fact that the effect of the elevated roller is observed not only for liquid nitro esters, but also for azides of lead and calcium, naturally, one should connect with the relatively high combustibility of the latter, significantly greater at increased pressures, than other studied explosives. Apparently, this is stipulated by the fact that the energy content in the compressed air, is very low and for ignition of difficultly combustible explosives it is insufficient.

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[1] Tablets obtained by weak pressing of a weight from hand through glass pipe.

One should indicate that the effect of an elevated roller is very close to that, which Bouden studied [3] in experiments with a striker, having a hole with a border around it.

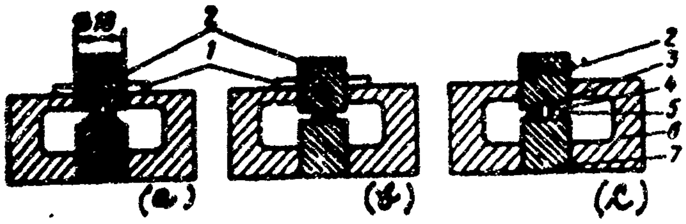

Fig. 3. Diagram of location of parts of the instrument in experiments for explaining the influence of a hole on the appearance of explosion at impact.

a—border of hole only touches a drop of substance, b—upper roller without hole only touches a drop of substance, c—upper roller is lowered and border of hole stands on lower roller, 1) spring for fixation of roller on definite height, 2) upper brass roller, 3) hole, 4) border, 5) drop of substance, 6) connecting piece with cutout, 7) lower steel roller.

We conducted a series of experiments with such a striker. The results obtained are in Table 2. Diagrams of the location of parts of the instrument and peculiarities of its design in these experiments are presented in figures 3 and 4.

The experiments confirmed the observations of Bouden about the high frequency of explosions of nitroglycerine in such conditions (Table 2, series of experiments 1—2). For obtaining of high frequency it is necessary, however so that the upper roller is lifted to a certain height above the lower, so that the edge of the border is above a drop of the explosive or at least within the limits of the drop, as in Fig. 3a. If the upper roller with hole is lowered to the lower one (Fig. 3c), then the high frequency of explosions is not observed (Table 2 series of experiments 4—6).

It is possible that the action of air in the hole in this case is not exhausted by its compression and heatup. We attempted to check this, placing nitroglycerine in a cup of plastic material (an alloy of bees wax and gun lubricant) and subjected it to impact by a roller with a hole and without it in instrument No. 1 with a small gap, filled with the same alloy (Table 2, series of experiments 7—9, Fig. 4a and 4b). In these conditions there should occur only compression of bubbles; flow of the explosive was hampered large resistance to flowing of viscous material in narrow gaps between roller and connecting piece; however in these experiments of such influence of a hole, which was noted in experiments with a connecting piece, arranged on the type of instrument No. 4 (Fig. 4c and 4d), was not fixed and the frequency of explosions was high both with the hole, and also without it.

Table 2

(See Table 2 On Following Page)

Table 2

Influence of mechanism of instrument and conditions of impact on frequency of explosion of nitroglycerine

(1) № серий опытов	(2) Навеска ВВ мг	(3) Груз г	(4) Высота падения груза см	(5) Число взрывов / Число опытов (6)	(7) № фигуры, иллюстрирующей расположение деталей прибора
I. Повышенная частость взрывов при наличии на торце верхнего ролика лунки с бортиком (верхний ролик приподнят над нижним и лишь касается капли нитроглицерина)					
1	4	260	50	9/10	3а
2	4	260	50	0/10	3б
3	4	2000	25	5/5	3а
II. Низкая частость взрывов при ролике с лункой и бортиком, но опущенном до касания с торцом нижнего ролика					
4	4	260	115	0/5	3в
5	4	2 000	25	2/9	3в
6	4	10 000	25	1/3	3в
III. Отсутствие влияния лунки с бортиком при затрудненных условиях течения ВВ					
7	40	260	50	2/2	4а
				2/2	4б
				0/3	4в
				3/3	4г
8	40	260	10	3/5	4а
				2/5	4б
				0/3	4г
9	50	260	10	9/10	4а
				6/10	4б
				0/10	4в
				0/10	4г

1) No. of series of experiments; 2) Weight of explosive in milligrams; 3) Load, g; 4) Height of fall of load, cm; 5) Number of explosions; 6) Number of experiments; 7) No. of figure, illustrating the location of parts of instrument.

I. Increased frequency of explosions with the upper roller having a hole with a border on the end (upper roller is raised above the lower one and only touches the drop of nitroglycerine)

II. Low frequency of explosions using a roller with a hole having a border, but lowered until it touches the end of the lower roller

III. Absence of influence of hole with border at hampered conditions of flow of explosives.

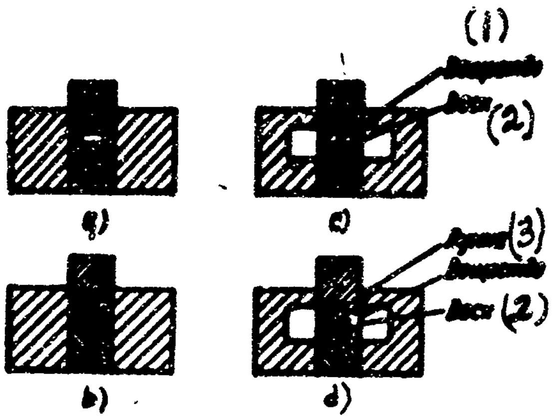

Fig. 4. Diagram of location of parts of a device in experiments illustrating the absence of the influence of a hole in hampered conditions of the flow of an explosive.

a) upper roller without hole, device No. 1, b) upper roller with hole, device No. 2, c) upper roller without hole, coupling with groove, d) upper roller with hole, coupling with groove.

1) Substance; 2) Wax; 3) Hole.

If we exclude the fall of nitroglycerine in a gap (experiments in instrument Fig. 4c and 4d), then the frequency of explosions in the absence of a hole is sharply decreased. Consequently, the hole by itself in these conditions is less effective than a narrow gap.

Due to the fact that nitroglycerine is very sensitive to impact, if it is given the possibility to leak into a narrow gap, and was not checked, then the effect of a hole in the absence of flow of this explosive at impact will be developed.

In light of these observations it is probable that with a roller having a hole, as in the case of a flat roller, an essential role is played by the flowing of compressed and heated air through the narrow gap between the border hole and the lower roller. The fact that such a flow takes place, is shown by the experiments of Bouden [5], which connected it with an explosion in the hole; in our experiments flowing with a breakthrough of the border of the hole was observed also upon replacement of nitroglycerine to an inert liquid. The tense flow of nitroglycerine upon crushing it through a narrow slot, which can promote the air bubble compressed in the hollow, apparently, is the main cause of the light appearance of an explosion in these conditions.

On the whole the described observations once again show the variety of ways, that the energy of a mechanical action can be concentrated in an explosive to a degree, sufficient for the appearance of explosion. The magnitude of energy, necessary for excitation of an explosion, is very small and constitutes an insignificant fraction of the total energy of impact. Therefore a decisive role for the appearance of an explosion can be played not so much by the energy of the action, but its distribution in the explosive. In those conditions, which especially favor concentration of energy, an explosion can appear from very weak influences.

Let us add that the conditions of impact, which are considered in this article, are completely real and in production. In connection with the fact that these conditions simultaneously are quite specific, it is possible that precisely their accidental reproduction also was the cause of some of the sudden explosions, occurring in the manufacture nitro esters and explosives on their base.

Conclusions

The frequency of explosions of certain highly sensitive explosives (nitroglycerine, lead azide et al.) at impact is sharply increased, if the roller, transmitting the blow, is not placed on the substance, but is at a certain height above it.

This effect, apparently, is connected with the capture, compression flow of air, leading to ignition of the explosive.

Literature

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3. Bowden, F. P. et alii, Proc. Roy. Soc., 1947, A188, 291.

4. See for example Bowden, F. P. and Gurton, O. A., Proc. Roy. Soc., 1949, A198, 347.

5. Bowden, F. P. er alii, Proc. Roy. Soc., 1947, A188, 311.

Chapter 1 Article 6

Pages 81 - 88

K. K. Andreyev and Yu. A. Terebilina

6. Concerning the Question of Mechanism of Appearance of Explosion During Test of Sensitivity to Impact in a Roller Instrument

As was shown by the investigations of N.A. Kholevo [1], [2], explosion during impact on a drop hammer under test conditions in roller instrument occurs because of flow of the explosive compressed by the impact. Distinctions in the speed of movement of various layers of the flowing explosive stipulate the appearance of internal friction and local heat ups, leading to explosion.

According to Kholevo, in roller instrument No. 1 (Fig. 1), explosion usually appears not between the roller faces, but in the radial clearance between the roller and sleeve. This circumstance, if it had direct experimental confirmation, would serve as convincing proof of the decisive role of explosive flow in the process of triggering of explosion by impact on a drop hammer. Till now, however, the triggering of explosion in the radial clearance has been judged by indirect data, namely by the more higher frequency of explosions of flowing explosives in instrument No. 1 as compared to those in instrument No. 2. Results of these experiments allowed different interpretation. As it would have been possible to allow that the presence of the groove in instrument No. 2 leads to decreased resistance to the escape of the explosive from the space between the roller faces in consequence of which the pressure obtainable during impact is lowered, leading to an increase in the number of refusals. It was possible to allow also that in instrument No. 1 at the triggering of explosion there occurs a sharp (by 90°) change of direction of movement of the extruded explosive during its transfer from the space between the roller faces into the radial clearance. Additional basis in favor of the last assumption is contained in the results of experiments with nitroglycerine and certain other explosives in instrument No. 4[1], where the frequency of explosions is small, although thanks to the large diameter of the rollers the length of the path of explosive flow is the same as in instrument No. 1.

The goal of the experiments described below was to prove directly that the flow of explosive in the radial clearance of a roller instrument can lead to explosion. Side by side with this, the experiments should determine precisely why such flow leads to explosion. Finally, they allowed to detect that in the usual conditions of test on a drop hammer even organic nonexplosive substances are decomposed; this shows that flow during impact leads to significant heat ups.

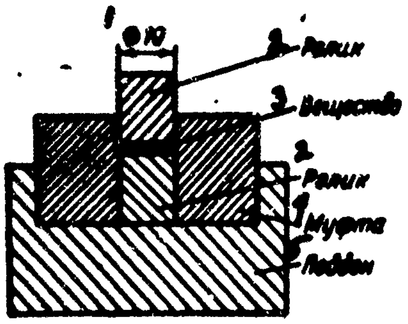

Fig. 1. Diagram of roller instrument No. 1 for test of sensitivity of explosives to impact.
1) F 10; 2) Roller; 3) Substance; 4) Sleeve; 5) Bottom plate.

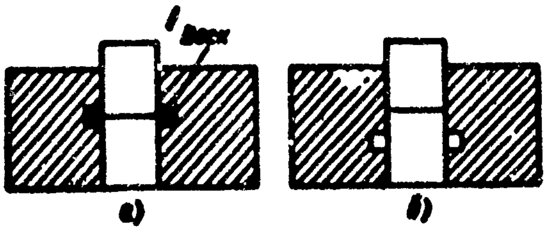

Fig. 2. Diagram of assembly of instrument No. 2 for appraisal of influence of change of direction of explosive flow on frequency of explosions:
a — groove of instrument, filled with wax; b — instrument in inverted view;
1) Wax.

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[1] See present collection, page 76.

Experiments On Ascertaining the Influence of Change In Direction of Movement of Explosive in Instrument No. 1

In these experiments two versions of assembly of instrument No. 2, shown in Fig. 2, were applied. In the first, the groove was filled with wax (Fig. 2a). It was natural to consider that the presence of the wax would soften assumed blow and would make less sharp the change of direction of flow from horizontal to vertical. In the second version (Fig. 2b) the sleeve was overturned and thus condition of charge flow near to those inherent in instrument No. 1 were created. Results of the tests are given in Table 1. With both versions of the experimental setup the frequency of explosions appeared practically identical (series 1 and 2). To this one should to add that the frequency of explosions of liquid and gelatinous nitroglycerine remained significant, if instead of instrument No. 1 an instrument prescribed by All-Union Government Standard 2065--43, with flats on the rollers (32% for liquid nitroglycerine with a sample of 0.03 g and 92% for 10%-leg gelatinous nitroblycerine with a sample of 0.05 g). In this instrument the change in the direction of movement was less sharp than with rollers without flats.

According to the series of these data one would conclude that a change in direction of explosive during test in instrument No. 1 does not render an essential influence on the results of the experiment.

Table 1

(See Table 1 on Following Page)

Table 1

Influence of explosive flow conditions on frequency of explosion of nitroglycerine and tetryl during tests on a drop hammer (load 10 kg, height of fall 25 cm, number of experiments per series 25)

1 № серий	2 Навеска *мг*	3 Зазор * *мк*	4 Условия и схема опыта	5 % взрывов	6 Средний отскок груза при отказах *см*
			7 Нитроглицерин. Влияние изменения направления течения ВВ на частость взрывов		
1	10	20	8 Фиг. 2а	24	16,0±0,5
2	10	20	8 Фиг. 2б	28	$16{,}3^{+0,8}_{-0,5}$
			9 Нитроглицерин. Влияние высоты верхнего зазора и заполнения нижнего зазора воском на частость взрывов		
3	10	27	10 Суммарная высота зазоров 18 *мм*; объем зазоров 8 *мм*³ Фиг. 3а	40	$16{,}5^{+1}_{-2}$
4	10	27	11 Нижний зазор заполнен воском; верхний зазор высотою 7 *мм*, его объем 3 *мм*³. Фиг. 3б	80	15,0±0
5	10	27	12 Нижний зазор заполнен воском; верхний зазор высотою 3 *мм*, его объем 1,3 *мм*³ Фиг. 3в c	68	$16{,}0^{+1,7}_{-0,5}$
6	2	27	13 Суммарная высота зазоров 18 *мм*, их объем 8 *мм*³ Фиг. 3а	0/15**	$17{,}0^{+0,5}_{-2}$
7	2	27	14 Нижний зазор заполнен воском; верхний зазор высотою 9 *мм*, его объем 4 *мм*³; 2 серии по 25 опытов Фиг. 3г d	40 12	17,0±0,5 17,0±0,5
8	2	27	15 Нижний зазор заполнен воском; верхний зазор высотой 7 *мм*, его объем 3 *мм*³, 2 серии по 25 опытов Фиг. 3б б	80 80	17,0±0,5 17,0±0,5
9	2	27	16 Нижний зазор заполнен воском; верхний зазор высотою 3 *мм*, его объем 1,3 *мм*³ Фиг. 3в c	40	17,0±0,5
10	2	27	17 Нижний зазор заполнен воском; верхний зазор высотою 2 *мм*, его объем 1 *мм*³ Фиг. 3в c	12	17,0±0,5

1) Number of series; 2) Sample, mg; 3) Gap,*microns; 4) Conditions and setup of experiment; 5) % explosions; 6) Average rebound of load at refusals, cm; 7) Nitroglycerine. Influence of change of direction of explosive flow on frequency of explosions; 8) Fig.; 9) Nitroglycerine. Effect of height of upper gap and of filling of lower gap by wax on frequency of explosions; 10) Total height of gaps 18 mm; volume of gaps 8 mm^3. Fig. 3a; 11) Lower gap filled with wax; upper gap height, 7 mm, its volume 3 mm^3. Fig. 3b; 12) Lower gap filled with wax; upper gap height, 3 mm, its volume 1.3 mm^3. Fig. 3c; 13) Total height of gaps 18 mm, their volume 8 mm^3 Fig. 3a; 14) Lower gap filled with wax; upper gap height 9 mm, its volume, 4 mm^3; 2 series of 25 experiments. Fig. 3d; 15) Lower gap filled with wax; upper gap height, 7 mm, its volume, 3 mm^3. 2 series of 25 experiments. Fig. 3b; 16) Lower gap filled with wax; upper gap height, 3 mm, its volume, 1.3 mm^3. Fig. 3c; 17) Lower gap filled with wax; upper gap height, 2 mm, its volume, 1 mm^3. Fig. 3c.

Table 1 (continued)

Продолжение

1 № серий	2 Навеска мг	3 Зазор* мк	4 Условия и схема опыта	5 % взрывов	6 Средний отскок груза при отказах см
			7 **Тетрил. Влияние высоты верхнего зазора и заполнения нижнего зазора воском на частость взрывов**		
11	20	40	8 Высота зазоров 18 мм Фиг. 3а	88	$16{,}7^{+0{,}8}_{-0{,}8}$
12	20	40	9 Нижний зазор заполнен воском; верхний зазор высотою 7 мм, его объем 5 мм³ Фиг. 3б B	72	$15{,}6^{+1{,}4}_{-1{,}1}$
13	20	40	10 Нижний зазор заполнен воском; верхний зазор высотою 2 мм, его объем 1,5 мм³ Фиг. 3в C	84	$14{,}8^{+2{,}2}_{-1{,}8}$
14	20	40	11 Нижний зазор заполнен воском; верхний зазор высотою 9 мм, его объем 6 мм³ Фиг. 3г D	80	14,0±2,5
15	50	40	12 Нижний зазор заполнен воском; верхний зазор высотою 7 мм, его объем 5 мм³ Фиг. 3б B	40	$8{,}6^{+8{,}9}_{-7{,}1}$
16	50	40	13 Нижний зазор заполнен воском; верхний зазор высотою 2 мм, его объем 1,5 мм³ Фиг. 3в C	28	$8{,}0^{+9{,}5}_{-5{,}5}$
17	50	27	14 Нижний зазор заполнен воском; верхний зазор высотою 7 мм, его объем 3 мм³ Фиг. 3б B	16	16,5±0,5
18	50	27	15 Нижний зазор заполнен воском; верхний зазор высотою 3 мм, его объем 1,3 мм³ Фиг. 3в C	20	$12{,}5^{+4{,}0}_{-10{,}6}$
19	50	27	16 Часть нижнего зазора заполнена воском Фиг. 4	72	12,7

1-6) same as Table 1; 7) Tetryl. Effect of height of upper gap and filling of lower gap with wax on frequency of explosions; 8) Height of gaps 18 mm. Fig. 3a; 9) Lower gap filled with wax; upper gap height, 7 mm, its volume, 5 mm³. Fig. 3b; 10) Lower gap filled with wax; upper gap height, 2 mm, its volume 1.5 mm³. Fig. 3c; 11) Lower gap filled with wax; upper gap height, 9 mm, its volume, 6 mm³. Fig. 3d; 12) Lower gap filled with wax; upper gap height, 7 mm, its volume, 5 mm³. Fig. 3b; 13) Lower gap is filled with wax; upper gap height, 2 mm, its volume, 1.5 mm³. Fig. 3c; 14) Lower gap filled with wax; upper gap height, 7 mm, its volume 3 mm³. Fig. 3b; 15) Lower gap filled with wax; upper gap height, 3 mm, its volume 1.3 mm³. Fig. 3c; 16) Part of lower gap filled with wax, Fig. 4.

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*Difference of Diameters of canal of sleeve and roller.

**Numerator = number of explosions, denominator = number of experiments.

Experiments With Limitation of Possibility of Escape of Liquid Explosive

For these experiments the instruments were set up by the diagrams shown in Figs. 3 and 4. In instrument No. 1 during the usual set up of experiments (Fig. 3a) liquid could flow through both the upper and lower gaps; the frequency of explosions constituted 40% (series 3). If the lower gap is filled with wax (Fig. 3b), the frequency of explosions is doubled (series 4); if the height of the upper gap is decreased from 7 to 3 mm (Fig. 3c), then even in this case the frequency of explosions, if it is decreased, it is insignificantly (series 5).

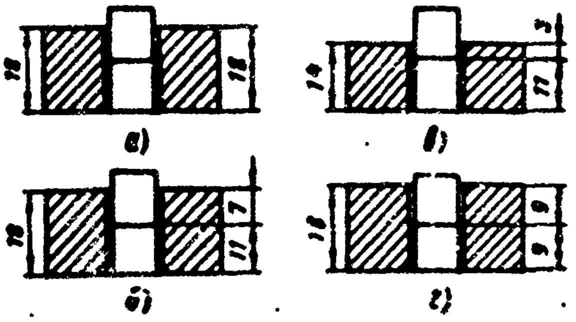

Fig. 3. Diagram of assembly of instrument No. 1 for determination of influence of limitation of escape of liquid explosive on frequency of explosions. a -- ordinary assembly; b -- lower gap filled with wax, height of upper gap 7 mm; c -- lower gap filled with wax, height of upper gap 3 mm; d -- lower gap filled with wax, height of upper gap 9 mm.

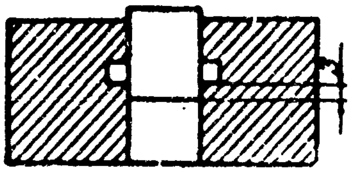

Fig. 4. Diagram of assembly of instrument No. 2 for clarification of influence of extrusion of explosive into groove on frequency of explosions.

A systematic study of the effect of gap height was conducted with the sample decreased to 2 mg. In these conditions in instrument No. 1, set up according to the diagram 3a, explosions did not occur (in 15 parallel experiments). Filling the lower gap with wax, at a height of the upper of 9 mm (Fig. 3d), increased the frequency to 12--40%. After a decrease in the height of the upper gap to 7 mm the frequency grew to 80%; repeated experiments gave the same result. A further decrease in the height of the gap, to 3 mm (series 9), lowered the frequency of explosions by twice; at a gap height of 2 mm it was lowered to 12%.

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It is interesting, however, that on increase of gap height to 9 mm led to a decrease in frequency of explosions to 12--40%. It is possible that in the last case the sample was insufficient to be extruded through the narrow part of the gap; it is not excluded that starting combustion of the explosive is extinguished by the subsequent lowering of pressure caused by the ejection effect.

Experiments with tetryl showed that it is less "sensitive" to height of gap and with a sample in 20 mg gave a frequency of over 80% both in the usual conditions of instrument No. 1, with filling of the lower gap with wax, and also with a decrease in the height of the upper gap to 2 mm.

An increase in the sample at a given gap led to a significant decrease in explosion frequency (series 15, 16 and 17[1]). It is possible that in the case of tetryl with its lesser fluidity (as compared to nitroglycerine) explosion appears between the roller faces, and the role of gaps reduces to securing a certain resistance to outflow. If it is too great, the exhaust velocity is small and explosion does not occur (large sample or narrow gap, series 18 and 19). If it is less, then explosions occur with great frequency. At a large gap (40 microns) and a sample of 50 mg, the height of rebound of load is almost twice less than with a sample of 20 mg. This shows that expenditure of energy on extrusion is great and in the first of these two cases is significantly larger.

Experiments in the Absence of Explosive Substance Between Roller Faces

The diagram of assembly of instrument for these experiments is shown in Fig. 5. Between the roller faces there is placed a layer of wax 0.5 mm thick, the lower gap is also filled with wax. In the upper gap a sample of nitroglycerine is introduced.

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[1] We will note one original observation. In experiments of series 19, conducted under conditions near to those of series 18, but distinguished by the fact that explosive was extruded not into the free space, but into the groove (see Fig. 4 and Fig 3c), the frequency of explosions strongly increased. Such influence of the groove had been shown frequently earlier; its cause is not wholly clear.

For this droplets of it are deposited in different places in the upper part of the sleeve channel; then, with slow turning, the upper roller is introduced, so that no nitroglycerine lands on the roller faces. Results of tests are shown in Table 2. The frequency of explosions of experiments of series 1 constituted 27%.

In the second series, wax was forced from the space between the faces by consecutive impacts to such an extent that rebound of load at impact was near to that obtained during control experiments (17.5 cm). The frequency of explosions in this case was even somewhat larger (40%), than in the preceding series.

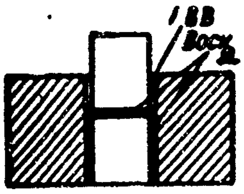

Fig. 5. Diagram of assembly of instrument No. 1 for determination of sensitivity of explosive located in radial clearance of instrument.
1) Explosive; 2) Wax.

During fourfold repetition of experiments in slightly different versions (with respect to thickness of wax layer, presence or absence of flats, size of sample explosions were also obtained with more or less frequency. This frequency was clearly larger in those conditions in which the rebound was larger, i.e., when higher pressures were attained.

In connection with by the fact that in the presence of wax between the rollers explosion is difficult to distinguish from refusal, there were conducted analogous experiments (series 3, 4 and 5) in a "gas" instrument (description given below), allowing more reliable judgement of the presence of explosion. Results of experiments in "gas" instrument appeared approximately the same as those in the first two series.

Table 2

Sensitivity of nitroglycerine when it is present only in the gap of instrument No. 1
(Weight of load 10 kg, height of fall 25 cm, number of experiments in series,25)

1 № серии опытов	2 Навеска нитроглицерина *мг*	3 Зазор *мк*	4 Условия опыта (Схема сборки прибора фиг. 5)	5 % взрывов	6 Средняя высота отскока груза при отказах *см*
1	2	27	7 Таблетка воска высотою 0,5 *мм*; нитроглицерин только в зазоре	27	5,0
2	2	27	8 Слой воска столь мал, что при ударе получается максимальный отскок, а воск при опыте в зазор не выдавливается	40	16,5
			9 Опыты в „газовом" приборе		
3	2	27	10 На торце находится таблетка воска весом 0,05 *г*. Верхний ролик от руки придавлен к воску	32	1,1
4	2	27	11 На торце ролика слой воска такой малой толщины, что получается максимальный отскок, а воск при опыте в зазор не выдавливается	56	16,0
5	4	27	12 Навеска нитроглицерина взята из расчета полного заполнения зазора	12	2,0

1) No. of series of experiments; 2) Sample of nitroglycerine, mg; 3) Gap, microns; 4) Experimental conditions (Diagram of assembly of instrument, Fig. 5); 5) % explosions; 6) Average height of rebound of load during refusals, cm; 7) Cake of wax, height 0.5 mm: nitroglycerine only in gap; 8) Layer of wax so small that under impact the maximum rebound is obtained; but during the experiment wax is not forced into gap; 9) Experiments in "gas" instrument; 10) Cake of wax weighing 0.05 g is located on face. Upper roller is pressed to wax from hand; 11) On face of roller there is a layer of wax of such small thickness that maximum rebound is obtained, but during experiments wax is not forced into the gap; 12) Sample of nitroglycerine taken from calculation of complete filling of gap.

Thus, the tests showed that in a roller instrument explosion under impact can occur in that case when there is no explosive between the roller faces but only in the gap between the upper roller and the sleeve.

It is natural to ask, in what way these explosions are triggered, both in general and especially in those cases when there is no substance between the roller faces that would be extruded during impact and lead to movement of the liquid explosive in the gap.

Most probably cause of this movement and explosion is the deformation of rollers, which take a barrel-like form under impact. In expanding they displace the liquid, forcing it to be pressed through the narrowed part of gap, where explosion occurs. This explosion can be spread into the adjacent, thicker part of the annular layer of compressed explosive. In confirmation of this assumption about the mechanism of triggering of explosion in the considered conditions, it is possible to point out that with replacement of the two rollers by one of twice the length (prepared from somewhat softer steel) during 15 experiments with a sample of 10 mg and a gap of 27 microns not one explosion occurred, also there were none in four experiments with a gap of 45 microns.

The fact that under impact in instrument No. 1 the flowing substance is subjected to sufficiently intense thermal influences is shown by experiments with wax, which formed a small cloud of smoke under impact. In order to estimate quantitatively the reaction proceeding under impact reaction, an earlier-developed "gas" instrument, allowing to measure the volume of gases formed at impact was applied. This instrument (Fig. 6) represents a chamber, having a mobile striker and aperture for exhaust of gases to a U-shaped manometer filled with dibutylphthalate; in the chamber is placed an ordinary roller instrument (in the given experiment instrument No. 1).

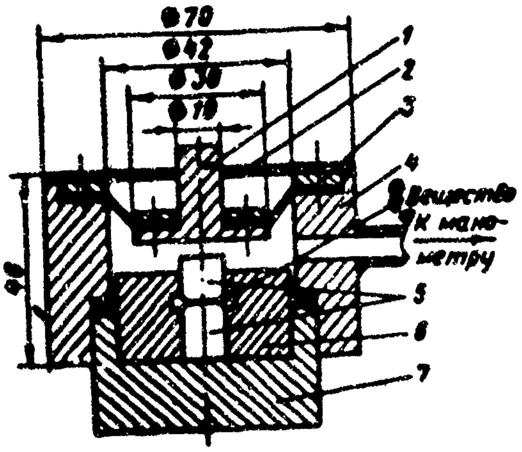

Fig. 6. Diagram of instrument for measurement of quantity of gases emitted during explosion.
1 — Striker; 2 — Cover; 3 — Rubber diaphragm; 4 — Housing; 5 — Rollers; 6 — Sleeve; 7 — Base; 8 — [test] Substance; 9 — to manometer.

The experiments showed that the wax is indeed decomposed under impact, forming about 20 cm^3 of gases per g. This confirms that heatups caused by mechanical influences under impact embrace noticeable volumes of the substance and are sufficiently strong to cause decomposition of even such a relatively thermally stable, nonexplosive substance as wax. Nitroglycerine, in which heatup caused by impact is a self-developed process, naturally will form much more (about 700 cm^3/g) gas in the case of full explosion.

From the whole of the considered data one should conclude that explosion of liquid explosive in a roller instrument under impact occurs quite differently than earlier investigators thought. The decisive factor of its appearance is the pressing of the substance through a narrow gap, which leads to the appearance of local seats of reaction. This reaction is developed to explosion, if there is near the seat a layer of explosive whose thickness exceeds the critical for propagation of combustion at a given pressure. It was just the failure to fulfill these conditions which led to the absence of explosions in the experiments experience in instrument No. 4 mentioned at the beginning of the article.

From the above it is also clear that those flow conditions that lead to the triggering of explosion in instrument No. 1 or in the GOST instrument, near to it in conditions of explosive flow, are very specific and therefore results of tests in them give only a very conditional characteristic of sensitivity of explosive.

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MT-63-254 Chapter 1 Article 7

Pages 89--93

K. K. Andreyev

7. On the Basic Factors, Determining the Danger of Explosives During Mechanical Action, and Methods of Its Estimation

In the last decade in presentations on the sensitivity of explosives to mechanical action there occurs radical shifts, which led to the change of experimental methods of its estimation. A main role in this was played by the work of N. A. Kholevo [4], [5], which uncovered the physical meaning of those phenomena, which lead to explosion upon impact by a drop-hammer. On this basis N. A. Kholevo showed and explained the great conditionality of results of standard and other methods of testing the sensitivity of explosives to mechanical action. These results characterize the sensitivity of an explosive (frequency of explosions) only in reference to those methods of deformation of charge, that are realized in the given method of testing, and cannot be transferred to another. From that time they offered many versions of the method of testing the sensitivity of explosives to mechanical action --on a drop-hammer and other instruments; in their totality they show that the frequency of explosions for one and the same explosive at a given energy of action can change in very wide limits. This circumstance very much hampers a practical estimate of the possibility of use of different technological methods in reference to that or another explosion. One of the main causes of this difficulty is the lack of full knowledge about the character of actions, that an explosion is subjected to in technological processes. This difficulty can be to a certain extent avoided, comparing the experience of practice, characterising to a known degree the danger of different operations in reference to separate explosives, with danger (sensitivity) of the latter in various conditions of laboratory testing.

Such a comparison can be used also for an opposite conclusion —the danger of those or other new technological methods or processes for known or new explosives on the basis of the behavior of the latter at different laboratory tests.

We know that for excitation of an explosion at impact it is necessary so that, in the first place, as a result of mechanical action there is a focus of warm-up and, secondly so that the reaction starting in it is developed into combustion or even explosion. The appearance of a focus of warm-up is connected with the mechanical properties of the substance, the development of the reaction in it to a large degree depends on the kinetic and thermochemical characteristics of the explosive.

It is relatively easy to answer the question about which of these characteristics determine the danger of the explosive. They can be reduced to two integral indices —inflammability[1] and sensitivity to detonations, which approximately can be characterized by both critical diameters —for combustion, from which the explosion usually starts at impact and for detonation.

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[1] One should indicate that inflammability depends not only on thermokinetic properties of the substance, but also on pressure. Therefore, the sensitivity of a given explosive also can be changed very much, depending upon under what pressure in its warm-up appeared. Experimental data on inflammability are meanwhile only for relatively low pressures. At present its study is conducted here at high pressures by the method of determination of critical diameters for combustion. We add that at least for low pressures, both for individual explosives, and also for mixtures a parallelism is not observed between the critical diameter for combustion and for detonation. Thus, black powder (all components of which separately are not explosive) burns easily at small diameter of charge, but its detonation is not described in literature; PETN easily detonates (critical diameter of detonation 2 mm), but poorly burns (critical diameter of burning 30 mm at atmospheric pressure and nearly 4 mm at 25 technical atmospheres), amatols (critical diameter of burning of about 30 mm) burn poorly and detonate badly, dynammons burn much better than amatols, but detonate worse than them.

It is complicated to answer the question of which indices of mechanical properties lead to increased danger, in other words, other conditions being equal, is a more fluid or less fluid explosive more dangerous. In general form the answer to this question cannot be given, since there are concrete conditions, in which fluid substances are dangerous and others, in which less fluid substances are dangerous.

But still in most cases it is possible to consider a difficultly-flowing substance more dangerous. In reality for the appearance of warm-up is required sufficiently high speed of movement and pressure. If the substance is stubborn and difficultly-flowing, then the action of impact cannot be softened and there will appear large pressure, under which will start displacement of layers of the substance relative to one another (internal friction) or relative to the impact (external friction); it is natural that inflammability at large pressure will be great.

It is necessary here to bear in mind that in practical conditions, impact as a rule, acts under a certain angle (slanting or slipping impact). As distinguished from that, which occurs at impact by normals at drop-hammer testing, for example, in instrument No 1, in case of oblique impact the low fluidity of the substance cannot protect it from shifting. In this case displacement of layers of the explosive relatively to one another or relatively to impact is forced and it is no longer determined so much by fluidity, as much as tangential forces, acting at oblique impact. The qualitative border between impact and friction here is absent, but a quantitative relationship is determined by an angle, under which the impact occurs; on it in combination with fluidity and coefficient of external friction depends the relationship of tangential and normal efforts.

Tests for sensitivity to friction are distinguished from impact tests by normals only by the fact that at friction, normal and tangential forces rely independently from each other.

In spite of the fact that upon testing sensitivity to friction, the stresses are usually less than the more dangerous substances in which inflammability is great, i. e. the critical diameter even at slight pressure is small; for example, black powder, mercuric fulminate, some pyrotechnical compounds, etc.

Substances,easily-flowing due to the small coefficient of internal friction or difficult-to-burn (great critical diameter), are not very sensitive to friction; for explosion of such substances it is necessary to have a large pressure. Precisely by both of these causes trotyl belongs to a number of explosives relatively not dangerous in processing, then as lead azide or hexogen --to a number of relatively the most dangerous. It is natural also that the danger of the last can be decreased by an increase of their fluidity which also is accomplished in technology --by applying a "lubricant" (flegmatizor) to particles of such explosives.

One should add that a flegmatizor, apparently, plays a role not only on the first stage of excitation of explosion by impact --the stage of appearance of warm-up at flow. It also inhibits <u>development</u> of focus of burning, softening thermal shock of hot products of transformation, that may cause cracking of neighboring particles of the substance and by this increase the surface of burning.

Once again we emphasize that these considerations are not universally applied --in a series of conditions excitation of explosion can be accomplished by other ways --for example igniting as a result of pressure and warm-up of a gas bubble (this pressure can be relieved, if the explosive is fluid), as a result of friction of solid particles of outside impurities in the explosive against each other, or friction of them against an anvil (shock object) etc. Besides, there can be special conditions of flow, when very large or conversely very small fluidity can add to the large frequency of explosions --then trotyl can be more sensitive than lead azide or ammonium nitrate more sensitive than nitroglycerine.

An estimate of the danger of concrete industrial processes can be therefore performed only at full knowledge of the character of those actions, to which the explosive is subjected; in the absence of such knowledge it is necessary to conduct a test with modeling of real influences.

On The Most Expedient Laboratory Methods of Estimating The Sensitivity of Explosive Substances To Mechanical Actions

There appears the question, which of the existing experimental methods of determination of sensitivity in the greatest degree reflect the danger of the substance during mechanical actions, if we proceed from the above-considered general considerations.

Drop-hammer tests in different versions [4], [5] (instruments No 1, according to GOST 2065-43 and No 2, and also a modification of the last) have that principal shortcoming that it characterizes chiefly the possibility of appearance of focii of reaction, but not propagation of the process. In principle the weak side of this test is also that the possibility of flow and its conditions in a significant degree are determined by the fluidity of the substance.

If the substance is very low-fluid like lead azide, then it is not exploded in one of the three instruments above-mentioned; if it is too fluid, then it is only with difficulty, at very narrow gaps, exploded in instrument No 1. At the same time in practice fluidity plays, as was noted above, a significantly smaller role.

In testing explosives for so-called sensitivity to friction, when an impact transfers plates, among which is included the explosive, friction takes place independently of fluidity of the substance, although it also has an influence on the character of friction, caused by dislocation of plates. This circumstance is an essential advantage of the given method as compared to the drop-hammer test.

If fluidity of the substance is great, then is required, apparently, a very large pressure and certain subsidiary conditions so that in testing the sensitivity to friction an explosion would occur. Therefore, in Bowden's experiment[3] in the instrument developed by him for testing the sensitivity to friction many explosives, as for example PETN, an explosion does not occur. At the same time these substances are easily exploded in the version of Bowden's instrument offered by V. S. Kozlov [1], where the explosive is pressed between the ends of two rollers: secured and mobile. At horizontal impact on the lateral surface of a mobile roller it, according to an idea ob V. S. Kozlov should be transferred according to the normals to its axis. In reality, since the durability of the connection of the upper end of the roller (steel--steel) and the lower (steel-explosive or explosive-explosive) are not identical, then the roller accomplishes movement along the arc. Here there appears not only friction, but also slipping impact. In fluid explosives friction of metal against metal also occurs. In these conditions even relatively easily-fluid explosives are exploded, including nitroglycering powder.

In combination with determination of inflammability (ability to burn) the results of a test on a pendulum instrument of V. S. Kozlov (K-44-III), apparently better than other methods, can characterize the practical danger of the explosive during mechanical actions.

This conclusion does not signify the needlessness of impact tests according to normals on a drop-hammer. However, these tests acquire an additional character, illustrating the behavior of the explosive at certain special conditions of mechanical action. In this respect from new methods one should especially note the test with raised rollers[2], that allows a very graphic representation of high inflammability, and this means the danger of an explosive in those conditions, in which it is not revealed by the usual drop-hammer test.

We emphasize once again that it is impossible to be limited at determination of sensitivity only by a test on the Bowden-Kozlov instrument without determination of the ability of the substance to burn and to detonate[1]. Although to a certain extent, the ability to burn and to detonate is self-developed in this test; but this occurs at indefinite and large pressures. At conditions of mechanical actions usual in practice, a large pressure is created only in a very small part of the volume, occupied by the explosive, a greater part of it is at relatively small pressures. Therefore determination of ability to burn preserves its most important value, and besides this, determination should be made in that area of pressures, which corresponds to practical conditions, since the ability of a substance to burning depends on pressure and besides for various explosives in various stages.

Conclusions

The fundamental properties of an explosive, determining its danger at mechanical actions, are the thermokinetic characteristics, developed in critical diameters for burning and for detonation.

The possibility of appearance at mechanical actions of burn-up and pressure, sufficient for excitation of burning, depends on concrete conditions of deformation and fluidity of the substance. Usually it is greater for difficultly-fluid substances and can be estimated by the action of slipping impact on V. S. Kozlov's instrument (K-44-III).

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[1] As an illustration of this conclusion we indicate that ammonium perchlorate in the test on the Bowden--Koslov instrument provides a high frequency of explosions; its ability to burn is very low (critical diameter 33 mm) which confirms the small danger of perchlorate in circulation. Addition to perchlorate of fluid organic substances decreases sensitivity during the test on the Bowden--Koslov instrument, and the ability to burn greatly increases; this growth can obtain a predominant value which leads to the increase of danger in circulation of such mixtures as compared to pure perchlorate.

Literature

1. See K. K. Andreyev and A. F. Belyayev, Course of The Theory of Explosives, Def. Pub. House, 1960, page 323.

2. K. K. Andreyev and A. F. Belyayev, Course of The Theory of Explosives, Def. Pub. House, 1960, page 285. See also this collection, page 72.

3. F. F. Bowden and A. D. Ioffe, Excitation and Development of an Explosion in Solid and Liquid Substances, For. Lit., 1955, page 25.

4. N. A. Kholevo, Transactions of S. M. Kirov, Kazan Chemical-Technological Institute, 1946, 10, 91; 1947, 11, 116.

5. N. A. Kholevo, Collection "Physics of Explosion", Academy of Sciences, USSR, 1955, No. 3, page 16. See also this collection, page 5.

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K. K. Andreyev

8. On Certain Foreign Investigations in the Methodology of Experimental Determination of Sensitivity of Explosives to Impact

Of all the characteristics of explosives, sensitivity to impact has always been one of the least definite. This uncertainty stems from the question of what kind of indices of impact -- general energy, pulse, speed or any other -- should be considered as the factor determining the triggering of explosion.

Typical for data on sensitivity are large variations between results obtained by various investigators for the same explosives.

Finally, test of sensitivity to impact is only one of the tests of explosives for which the recommended number of parallel experiments will attain 25--100; with this, as a characteristic of sensitivity usually is taken the frequency of explosions at a given energy of impact or that energy at which the frequency of explosions equals ½ or some other specific value.

The opinion was wide spread that variability of sensitivity is combined only with secondary factors--hard-to-remove defects in the methodology of determination on a drop-hammer and that if they could be avoided, then it would be possible to establish sensitivity as a certain absolute constant of a given explosive. Echoes of these moods are found in particular in reflections in the 1955 conference on questions of sensitivity of explosives. In a series of proposals it was repeatedly underlined (and this was reflected even in decisions of the conference) that sensitivity is an objective property of explosives, as if facts indicating the changeability of sensitivity, the dependence of frequency of explosions on conditions of action[1] and the conclusions of those investigators also stopped to consider these facts as accidental, secondary, and uncovered their physical meaning, are attempt at a materialistic understanding of this physical phenomenon.

Radical change of theories on sensitivity was realized by N. A. Kholevo, showing that danger of triggering of explosion during mechanical influences on an explosive depends on its thermokinetic characteristics as determined by its chemical structure, on its mechanical properties, and on conditions of impact which one by no means exhausted by the energy of the latter. Due to this, the danger of explosion at a given magnitude of impact energy can, for a given explosive, change in very wide limits, and it is senseless to search for a universal absolute characteristic of danger of a given substance detached from conditions of impact.

We will not remain here more specifically on the theories and results of experiments of N. A. Kholevo, inasmuch as they are illuminated in a series of articles [2], [3].

The opinion of N. A. Kholevo, however, did not at once receive the proper acknowledgement among investigators, from many of whom it was difficult was to erase the old, incorrect, but habitual view on sensitivity. Later in a number of countries (The USA, Sweden, Germany) works were published whose authors arrive at conclusions, analogous to those of N. A. Kholevo. Consideration of these works is the purpose of this article.

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[1] Incidentally, the strongly expressed statistical character of results of tests on sensitivity already by itself indicates the large dependence of results of experiments on changes in their conditions so small that they are outside the control of the experimenter.

Ideas On Sensitivity Of G. B. Kistiakowski and R. Connor (USA)

During the Second World War the prominent American physicists G. B. Kistiakowski and R. Connor worked on the investigation and development of explosives. With respect to sensitivity of explosives to mechanical influences they naturally turned to the methods of its determination, used in civil (Bureau of Mines) and military (Pikatin arsenal) establishments in the USA. However Kistiakowski and Connor quickly were convinced of the unfitness of these methods for absolute characterisation of sensitivity and, moreover, in the impossibility of obtaining of such a characteristic. Not describing the experimental data that led them to this conclusion, they formulate it in the following positions, which are given literally.

"It was shown that for triggering of explosion necessary a fast impact, causing movement of particles and friction between them is necessary. Apparently, the surface of particles should be locally heated to high temperatures. An equally important factor is also closure (confinement) of the substance. Conditions should be such that the gasiform products of the initial reaction cannot escape. Otherwise for triggering of explosion a much larger mechanical effort must be expended.... Local ignition, caused by impact on a few small sections of surface, must be supported by means of retention of hot gasiform products by this surface. Then, increasing local pressure accelerates the reaction and explosion occurs. Otherwise initial ignition can easily die out." [6].

And in another place:

"As a result of investigations, however, it was determined—and this is a discovery of significant practical importance,—that it is impossible to find such a characteristic, as a definite mechanical sensitivity of an explosive. Indeed, by changing test conditions it is possible to change even the order of mechanical sensitivities of explosives."

These positions are in complete agreement with the conclusions made by N. A. Kholevo prior to publication of the American work. One should to add that conclusions of American investigators were published in their book "Science in the Second World War", which apparently, is little known to European investigators and in particular by those of them, whose works are considered below. This lack of information refers probably and/relates also to works of N. A. Kholevo, published for the first time in the News of the Kazan Chemical-Technological Institute imeni. S. M. Kirov in 1946--1947.

Work of Ljungberg (Sweden)

The next country, in which were "discovered" and developed the ideas of N. A. Kholevo, was Sweden.

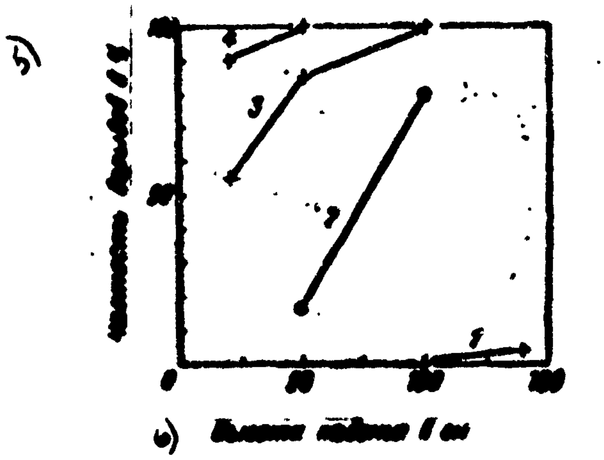

Fig. 1. Frequency of explosions of nitrogelatin in instruments No. 1 and 2 according to Ljungberg. (Load 2 kg, thickness of explosive layer 0.4 mm, faces of rollers polished, number of experiments in series 25). 1--instrument No. 2, 2--instrument No. 1, 3--instrument No. 2 with one circle of filter paper, 4--instrument No. 2 with two circles of filter paper, 5--Frequency of Explosions in %; 6--Height of fall in cm.

In the work of S. Ljungberg [4] is investigated the triggering of explosion under impact in instruments analogous to instruments No. 1 and 2 of N. A. Kholevo, i.e., during the absence or presence in the guide sleeve of an annular groove, where the **explosive** can flow. Results of experiments with nitrogelatin are presented in Fig. 1. In instrument No. 2 with a two-kilogram load separate explosions were observed only starting from height of fall of 1.4 m. In instrument No. 1 with a gap 0.05 mm[1] and 0.5 and 1-m heights of fall of load, the frequency of explosions was significantly greater. If between the explosive and the face of the roller one places a circle of dry filter paper or a sheet of asbestos from one or from both sides, then even at height of fall of 0.2 m a significant frequency of explosions is observed. If the paper is moistened by water, then explosions are not observed even with an increase in height of fall of load to 1.5 m. All these results natural are explained by the relatively great (for instrument No. 2) **fluidity** of nitrogelatin as a consequence of which high pressure is not created at impact. The hampering of escape by the application of paper or location of rollers in a sleeve without a groove increases pressure at escape, which leads to explosion.

If we apply rollers whose faces are not polished, but only ground, the frequency of explosions strongly increases even at low heights of fall of load, since escape of the explosive is hampered by the roughness of the face surfaces.

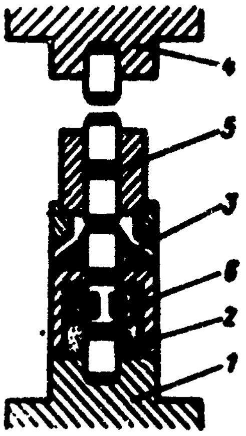

Fig. 2. Mechanism for measurement of pressure in time under impact on drop hammer.
1 -- anvil, 2 -- plexiglas insulation, 3 -- protective ring, 4 -- load, 5 -- explosive 6 -- tensometeric pickups.

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[1] Decrease of gap in case of nitrogelatin increases frequency of explosions.

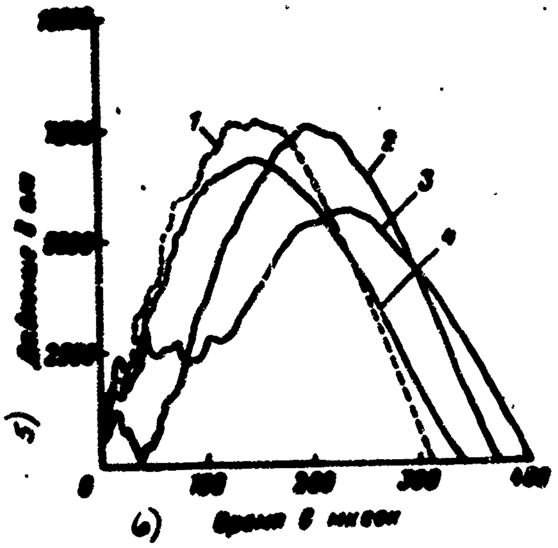

Fig. 3. Change of pressure in time in instruments 1 and 2 under impact on plasticine. (Load 2 kg, fall height 0.5 m; thickness of layer of plasticine, 0.4 mm; faces of rollers polished).
1--without plasticine: 2--with plasticine in instrument No. 2; 3--with plasticine in instrument No. 1 with diameters of sleeve channel and roller of 8.05 mm 8.00 mm respectively; 4--with plasticine in instrument No. 1 with diameters of sleeve channel and roller of 8.00 mm; 5--pressure in atm; 6--Time in microsec.

If we moisten ground faces with an inert liquid, then we obtain as low a frequency of explosions as with polished rollers. Powdery high-viscosity explosives, which are not extruded even with polished faces, are less sensitive to state of surface.

With the help of the mechanism depicted in Fig. 2, the change in time of pressure under impact was determined on a cathode oscillograph by tensometeric pickups. Without explosive or with its layer mechanically homogeneous and completely confined, impact has an elastic character. If the layer consists of a plastic substance, capable of being extruded, then during extrusion, as long as it is incompleted, impact has a nonelastic character. Duration of extrusion depends on dimensions of apertures through which the discharge escapes, the viscosity of the explosvie and pressure.

In Fig. 3 are shown curves obtained for an 0.4 mm layer of plasticine with polished faces and height of fall of load of 0.5 m. With roller and sleeve-channel diameters of 8.00 mm the possibility of flowing of the substance was practically removed and curves, without and with plasticine, are very similar, with the only distinction being that the maximum pressure in the last case is somewhat less, and duration of blow greater (curves 1 and 4).

With a sleeve channel of 8.05 mm is observed a period of extrustion in which impact is not elastic; behind it there follows a section of elastic impact (curve 3).

In instrument No. 2 at first is observed a small rise in pressure, completed after 35 microsec after this time the plasticine is extruded and the subsequent path of curve is almost the same as that without plasticine (curve 1). In Fig. 3, for experiments on instrument No. 2 (curve 2), the beginning of impact is not seen, since the duration of extrusion of an 0.4 mm layer in another experiment, at a height of fall of 1 m, was greater than 125 microsec. Thus extrusion continued for more than 90 microsec before the increase of pressure became sufficient for registration by its oscillograph.

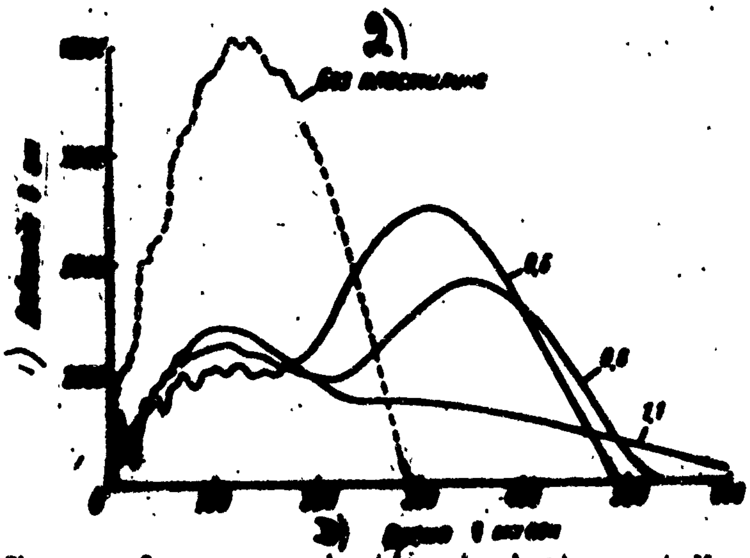

Fig. 4. Change of pressure in time in instrument No. 1 during impact on plasticine, depending upon the thickness of its layer. (Load 2 kg; height of its fall,1 m; diameters of canal sleeve channels 8.05 mm, and of roller 8.00 mm; roller faces polished). Numbers by the curves indicate the thickness of layer of plasticine in mm.
1—Pressure in atm; 2—Without plasticine; 3—Time in microsec.

In Fig. 4 are depicted curves of change of pressure in time for plasticine at different layer thicknesses. With an increase in the thickness of the layer the time of extrusion increases, and the duration of the elastic part of the blow is less. Maximum pressure during extrusion is approximately the same as that at a height of fall of 0.5 m, and is, apparently, characteristic for flow of plasticine at a given dimension of gap.

For nitrogelatin considerably distinguished from plasticine in fluidity, on analogous curves the period of extrusion is expressed less clearly. In Figures 5 and 6, where results are presented of experiments with nitrogelatin in instrument No. 2 with an explosive-layer thickness of 0.4 mm and height of fall of load of 1 m, we note only a small increase of pressure which is finished after approximately 40 microsec. Extrustion would have to continue for at least 50 microsec before the oscillograph would begin to mark pressure, and with this the thickness of layer would have to become less than 0.1 mm. Forty microsec later, almost all the explosive was extruded, and the subsequent change of pressure in time had the same character as that during elastic impact without explosive.

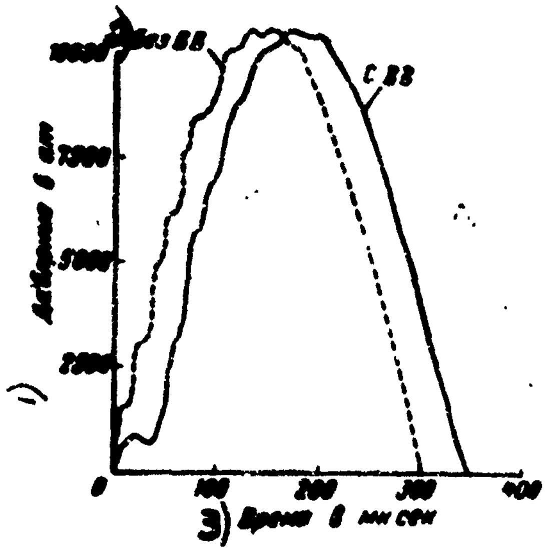

Fig. 5. Change of pressure in time in instrument No. 2 during impact on nitrogelatin. (Load 2 kg, height of its fall 1 m, thickness of explosive layer 0.4 mm, roller faces ground).
1--Pressure in atm; 2--without explosive; 3--Time in microsec.

In experiment with explosive there was no explosion.

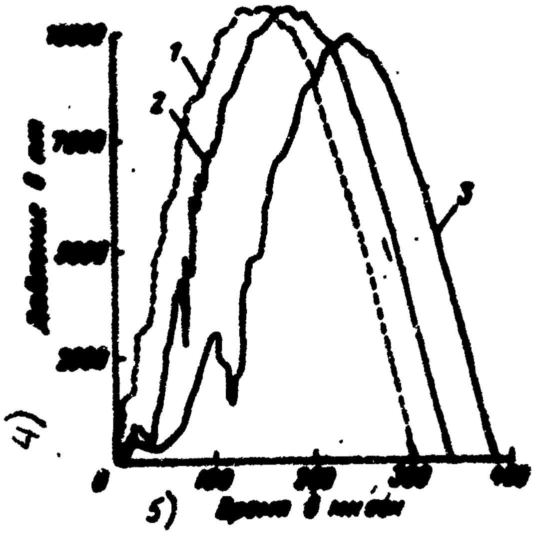

Fig. 6. Change of pressure in time in instrument No. 2 during impact on nitrogelatin. (Load 2 kg, height of its fall 1 m, thickness of explosive layer 0.4 mm).
1--without explosive, 2--with explosive, roller faces ground, 3--with explosive between two paper circles, of roller faces polished, 4--Pressure in atm, 5--Time in microsec.

In experiment with explosive explosions occurred.

Curves for experiments with an 0.4 mm layer of nitrogelatin and ground faces without explosion (Fig. 5) and with explosion (Fig. 6) are very similar. On ascending part of last curve a transient minimum and several small disturbances of its path are seen. Similar influence of explosion was observed with location of the 0.4 mm layer of nitrogelatin between two paper circles with ground roller faces (curve 3, Fig. 6) the only distinction being that minimum of pressure was expressed more clearly. In both cases the duration of explosion was small as compared to the time of impact, which agrees with observations of Rideal and Robertson [7].

With ground faces (as distinguished from polished) explosive remains in deepenings of surface, when its ridges make contact and pressure is increased. With this large local pressure appears at points of contact and, possibly, with this, as a result of plastic flow of metal, heatup will be formed, igniting the explosive.

In experiments with nitrogelatin along pressure — time curves it is very difficult to establish, whether explosion had a place. The latter appears in the form of transient oscillations of pressure on ascending branch of curve, but frequently these oscillations are no different than random ones.

In order to establish the moment of explosion, the glow appearing as a result of it is directed through a special aperture in the sleeve onto a photocell. Such a system of recording is not perfect, since the point at which explosion appears, registered on the pressure — time curve may not be visible through the aperture directed on the photocell. In Table 1 are given several values of the time from beginning of increase of pressure to explosion. Delay of explosion diminishes with an increase in height of fall. With ground roller faces the moment of ignition approximately coincides with moment of completion of extrusion of the explosive. During experiments on a drop-hammer of different construction cases of appearance of explosion after termination of impact were observed. This, apparently, was connected with the fact that a certain time was required for development of explosion.

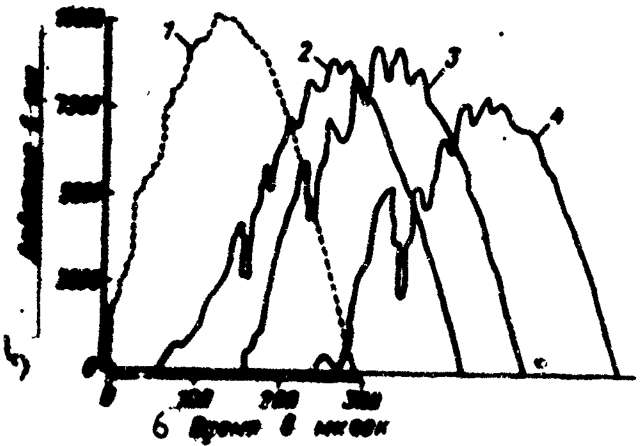

Fig. 7. Change of pressure in time in instrument No. 2 during impact on nitrogelatin and powdered trotyl and PETN. (Load 2 kg; height of its fall 1 m; thickness of layer of nitrogelatin 0.4 mm, trotyl and PETN 0.2 mm; faces of rollers polished).
1—without explosive; 2—nitrogelatin between two paper circles; 3—trotyl; 4—PETN. Curves are displaced along axis of time. 5—Pressure in atm, 6—Time in microsec.
In experiments with explosives explosions occurred.

Analogous experiments were set up with PETN and trotyl. As Fig. 7 shows, curves of change of pressure for these explosives were similar to each other and, in turn, analogous to curves observed with nitrogelatin located between paper circles.

Thus the experiments of Ljungberg confirm the conclusion of N. A. Kholevo that during impact on a drop hammer there occurs/ extrusion of explosive from the space between faces; the appearance or absence of explosion depends on resistance to this extrusion, determined in particular by the magnitude of the gap between roller and sleeve and also by the presence of groove, and, naturally on the properties of the substance. The pressure -- time curves obtained give concrete quantitative idea of this important characteristic of the process.

Time From Beginning of Pressure Increase to Explosion Table 1

1) Высота падения см	2) Скорость при ударе см/сек	3) Время мксек	4) Состояние торцов роликов
100	450	95—115	5) Полированные, с двумя бумажными кружками
50	310	170—185	
100	450	30—40	6) Шлифованные

1--Height of fall, cm; 2--Speed during impact, cm/sec/ 3--Time, microsec; 4--State of faces of rollers; 5--Polished, with two paper circles; 6--Ground.

Work of Koenen, Ide, and Haupt [5] (West Berlin)

A major experimental investigation in search of method of testing explosives for their danger in handling was conducted recently in the same laboratory (earlier the Chemical-Technical Institute, now Control of Testing of Materials), in which Castes at the beginning of the century developed contemporary method of determination of sensitivity of explosives to impact.

Statement of the Problem

German investigators underline the necessity of many-sided characteristics of susceptibility of explosives to one or another form of mechanical influence. Only by the sum of results of these many-sided tests is it possible to make conclusions on the danger of explosives. Single measure of this danger at present cannot be given. They correctly note also that it is necessary to distinguish the possibility of appearance of explosion under impact from the possibility of its propagation, at least for secondary explosives; the chance of; for initiating the latter is great, so that triggering of explosion, as a rule, signifies also its propagation.

Main method in Germany of determination of sensitivity of explosives to impact is the known method of testing them on drop hammers in caste stamping instruments. Caste, taken to this time to according to international agreement on railroad transportation for characteristic of explosiveness of substances. The index of sensitivity by this method is that minimum height of fall of a load of definite weight at which is observed at least one clear explosion in 6 attempts, though subsequent norms call for 4 experiments. Study of this method, and also its improvement was the subject of the considered work.

Check of Methodology of Caste

The construction of the stamping instrument corresponded to the general requirements of Lentz and Caste, namely: surface of the striker was determined by area and was constant in state, and the possibility of lateral displacement of the explosive and of friction, to which as was assumed by these authors, sensitivity of explosives completely different than to impact, was absent.

Components of stamping instruments used in the given work had dimensions and quality of metal shown in Fig. 8.

The investigators in their experiments expected to obtain confirmation of those results on sensitivity that were obtained by Caste in his time. Taken as one of the most sensitive explosives was nitrocellulose (13.3% N), which according to Caste gives explosions with the fall of a 5-kg load from a height of 5 cm. Besides, it was expected that, in accordance with general views of Caste on the growth of number of explosions with height of fall of load, at 40 cm all 6 experiments will give explosions.

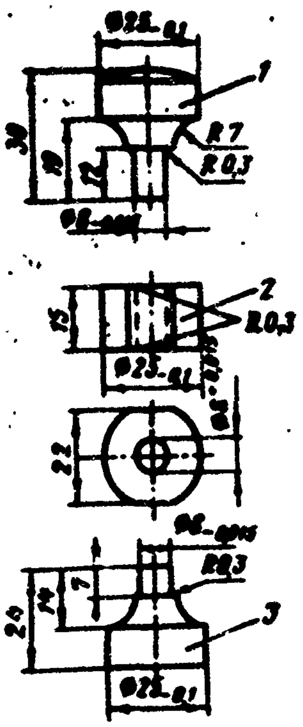

Fig. 8. Caste stamping instrument for determination of sensitivity of explosives to impact on drop hammer.
1--upper piston, 2--directing sleeve, 3--lower piston.
Material--tool steel (Beler extra MG), heat treatment--hardening and tempering to hardness of 60--63 Rockwell (scale C), working part of pistons and sleeve channel ground.

Despite these expectations at 10 cm not one explosion was obtained; at 20 and 30 only one, and at 40 cm not one; i.e., no growth in frequency of explosions with increase in height of load fall was observed. Since by tentative experiments the other explosives studied by Caste (collodion, tetryl, hexyl and picric acid) behaved analogously, the investigators moved to experiments with relatively more sensitive substances -- PETN and hexogen. In instruments of the described type and dimensions (gap 0.03 mm) in the entire range of heights from 10 to 40 cm with a 5-kg load not one explosion was obtained. With repetition of experiments with a decreased quantity of explosive (20 mm^3 instead of 50 mm^3) separate explosions were observed at 20 and 30 cm only with PETN -- hexogen did not give explosions.

Thus, the results of Caste and corresponding data of other investigators for PETN and hexogen could not be reproduced. This result is fully natural in the light of the investigations and considerations of N. A. Kholevo.

In order to understand fully how explosion is triggered, Ide and his collaborators decided to study the behavior of explosives during refusals and used for this purpose the little-sensitive dinitrobenzene and dinitrotoluene, and also trotyl. In new instruments -- with permissable, according to Caste, maximum energies of impact (i.e., 2 kg to a height of 60 cm, 5 kg to 40 cm, 10 kg to 24 cm, 20 kg to 16 cm), it was possible to observe that the substance during impact is pressed into a tablet and only in small part is forced into the gap; this part changes somewhat, depending upon magnitude of gap, weight of load, and height of fall. Under more intense action -- for example with a load of 10 kg and a fall of 50 cm (quantity of substance 50 mm^3) -- the substance was mostly forced through the gap and appeared on the lower side of the piston heads. In experiments with dinitrobenzene, part of the extruded substance on the surface was weakly tinted a greyish color, i.e., apparently, the substance was strongly heated and decomposed. During experiments with trotyl, in one or two places on the piston faces were observed flashes, which with the flow of the substance were propagated in the gap and through it outwordly. Application of thermosensitive substances, undergoing nonreversible changes of color at the achievement of a definite temperature, showed that coloring did not change between the piston faces. The substance thrown out from the gap not only was melted (temperature of melting 61°), but also changed color.

It is especially difficult to avoid extrusion of substance into the gaps in case of liquid and gelantinous explosives and, as a rule, the action of explosion is developed here not on surface the piston faces; with this, explosion appears the more easily, the less the instrument has been in use -- i.e., the less the gap between piston and sleeve channel.

Preventing the possibility of extruding the substance during impact strongly decreases the probability of explosion, so that even highly sensitive substances such as chloratite 1 or mercury fulminate are not detonated with the fall of a 2-kg load from a height of 60 cm.

With less accurate manufacture of the instrument or with its wear, the state of its working surfaces and piston edges is worsened. Influence of this impairment on behavior of an explosive during impact was checked as follows. In new instruments with small gaps (0.03 mm), smooth surfaces, and sharp edges, the piston faces were roughened by means of impact on a 20 mm^3 carbide of silicon, in one case and in another -- their edges were rounded (r = 0.5 mm) in order to make easier the explosive flow. These factors were also studied on old stamping instruments, whose gaps varied within the limits 0.2--0.5 mm. Finally with the help of a specially arranged sleeve which allowed the substance to leak also downwards, the gap was increased to 1 mm. As the explosive, fine-fibred nitrocellulose (13.4% N) was used; as was shown above, in normalized instruments this substance gives only single explosions.

Results of the tests are presented in Fig. 9. From these results it is clear that the least favorable conditions for explosion are presented by the normalized instrument, in which were observed only two single explosions. Under the other conditions (rough surfaces, rounded edges, increased gap) the probability of explosion is greater. Caste's rule that with an increase in height of load fall the probability of explosion is increased, in many cases is executed, however, only on the condition, that his requirement for the instrument -- small gap between piston and sleeve channel, smooth surface of faces, and impossibility of lateral extrusion of the explosive -- are not observed.

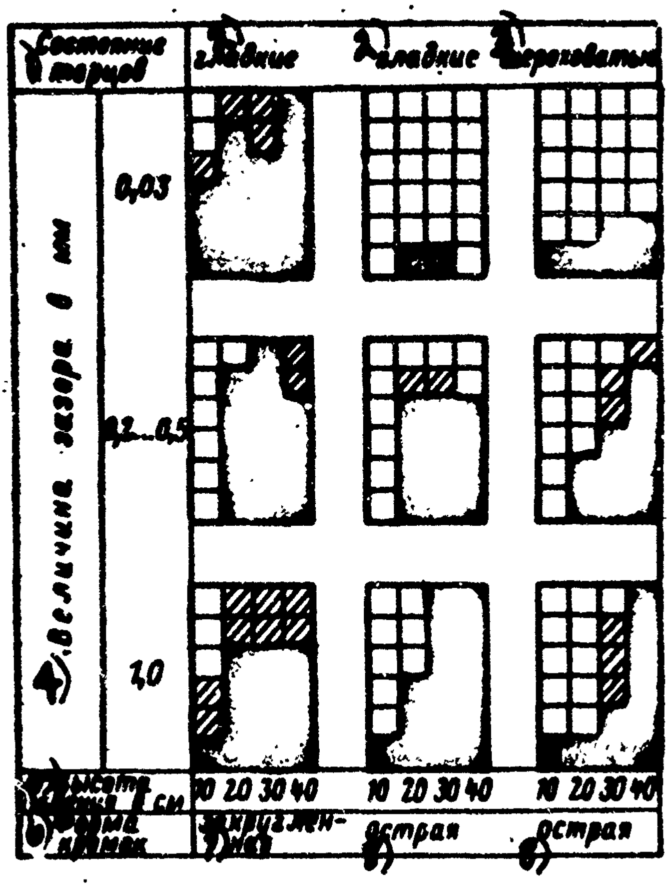

Fig. 9. Sensitivity of nitrocellulose (13.4% N, length of fiber about 0.5 mm) to impact on drop hammer in Caste instruments, depending upon state of surface of piston faces, form of their edges, and magnitude of gap between them and sleeve channel. (Load 5 kg, quantity of explosive 50 mm^3, number of experiments in each series 6).
Conditional designations: black block—explosion; shaded block—decomposition without sound; white block — no decomposition, no explosion.
1) State of faces; 2) smooth; 3) rough; 4) Magnitude of gap in mm; 5) Height of fall in cm; 6) Form of edges; 7) rounded; 8) sharp.

In order to clarify whether these observation have a general character, the experiments were repeated with a crystaline substance — PETN in the form of small particles. Results of these experiments, depicted in Fig. 10, are distinguished from those presented in Fig. 9 in that the transition from smooth faces to rough or an increase of the gap to 0.2—0.5 mm with smooth faces does not lead to an increase in the frequency of explosions, at the same time when under all remaining conditions a significant increase is observed.

These results confirm that a normalized instrument not useful for test of powdery explosives, inasmuch as even relatively sensitive explosives, when tested in it, do not display this sensitivity.

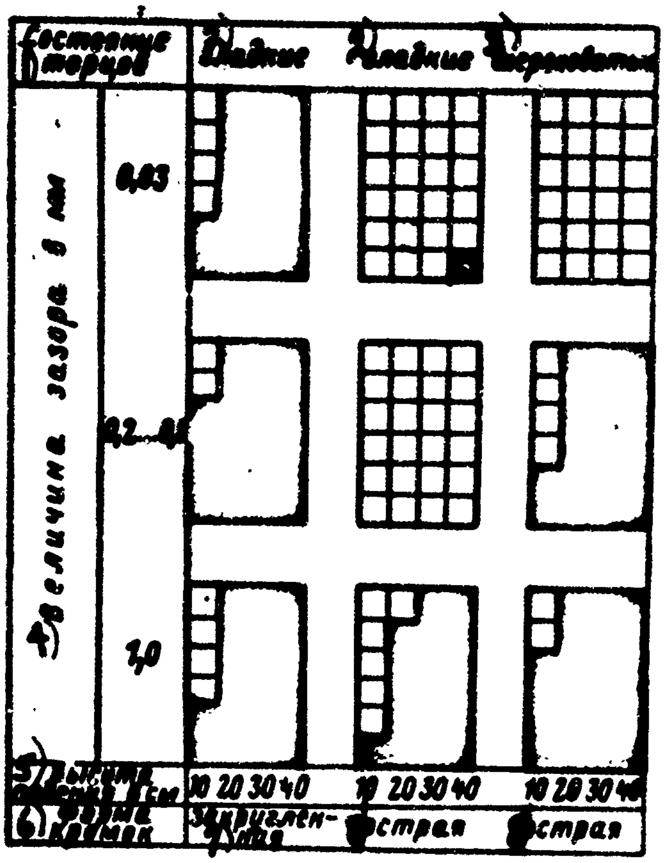

Fig. 10. Sensitivity of PETN (dimensions of particles 0.1--0.2 mm) to impact on a drop hammer in Caste instruments, depending upon surface state of piston faces, form of their edges, and the magnitude of the gap between them and the sleeve channel. (Load 5 kg, quantity of explosive 20 mm^3, number of experiments in each series 6).
Conditional designations--same as in Fig. 9; 1-8-same as in Fig. 9.

Experiments with PETN in the form of large particles (0.1--0.5 mm) showed its sensitivity to be high (Fig. 11); the presence of roughness gives a small increase in frequency of explosions, and an increase in the gap from 0.03 to 0.5 mm leads to explosions during almost every experiment. This yet again is different from the conclusion of Caste that with small dimensions of particles an explosive is more sensitive, with big particles.

Also experiments were conducted with liquid and gelatinous explosives. One of them was nitroglycerine, which was tested with load of 1 kg. Fig. 12 shows that behavior of a liquid explosive is completely different. For it the normalized instrument with smooth faces, small gaps, and sharp piston edges is exactly suited; in such an instrument the sensitivity of the explosive agrees with that indicated by Caste.

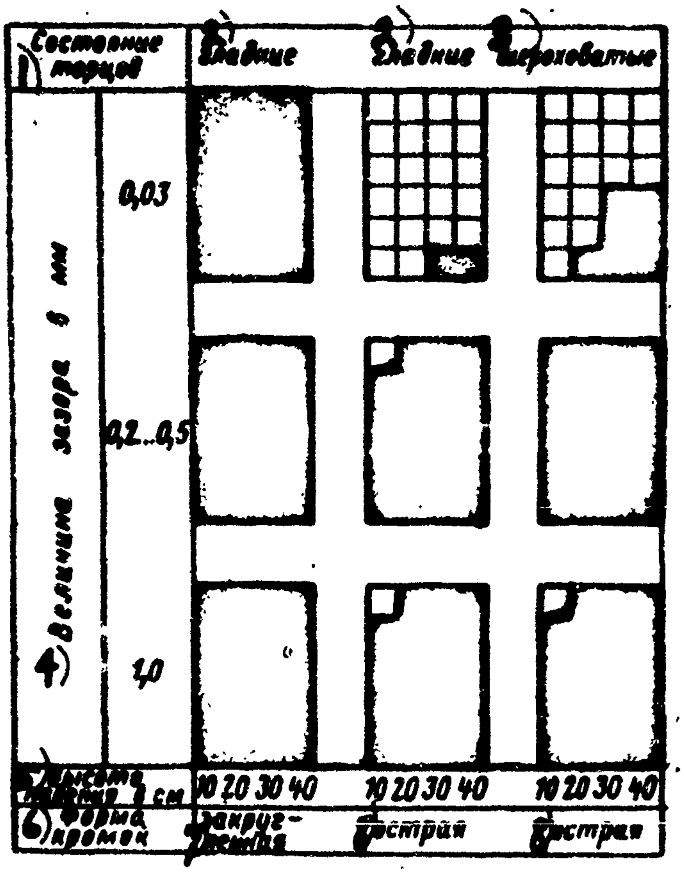

Fig. 11. Sensitivity of **PETN** (dimensions of particles, 0.1--0.5 mm) to impact on drop hammer in Gaste instruments under the conditions given in Fig. 10.
1-8-same as Fig. 9.

Presence of cants or roughness on the piston surface with a small gap leads to only one insignificant decrease of frequency of explosions of nitroglycerine; increasing the gap to 0.2--1 mm only with rough surfaces gives a significant **frequency** of explosions of this explosive; in other studied conditions explosions did not occur.

The investigators tested also gelatinous explosive--ammonia gelatin 1, having the following composition: 37.7% nitroglycol, 4% trinitrotoluene, 1.8% collodional cottons, 52.3% ammonium nitrate, 4% wood flour and 0.2 % prussion red. As tests results showed the dimension of the gap in this case plays a still larger role; its increase significantly decreases the frequency of explosions with other conditions being equal (see Fig. 13).

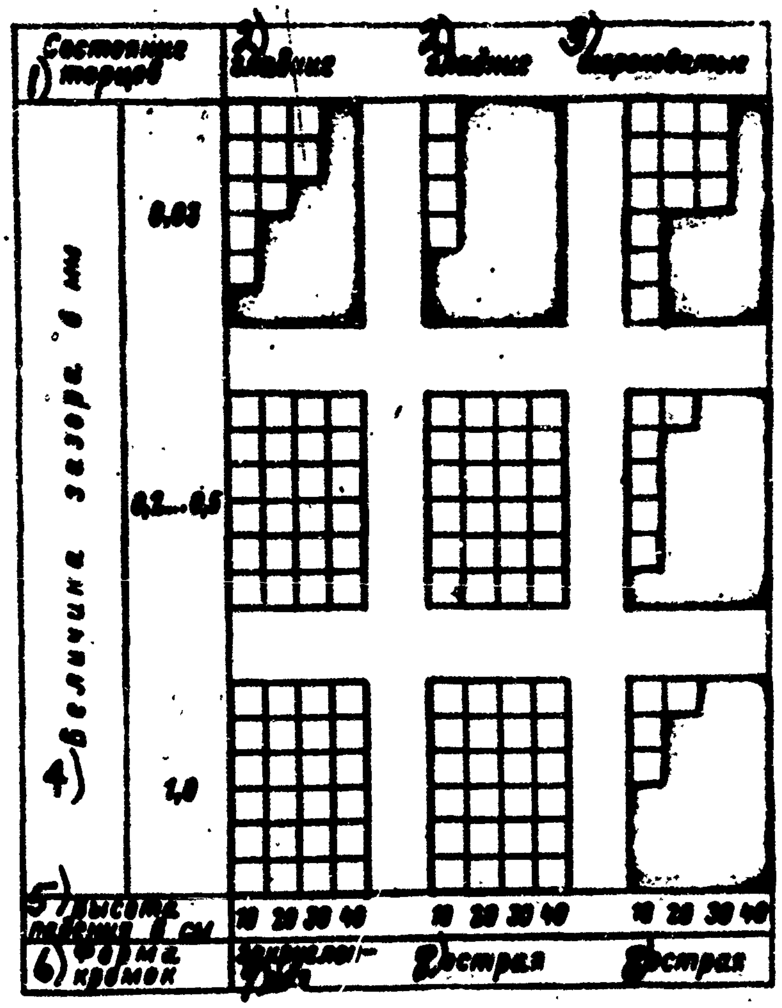

Fig. 12. Sensitivity of nitroglycerine to impact on a drop hammer in Caste instruments, depending upon state of surface of the piston faces, the form of their edges, and the magnitude of gap between them and the sleeve channel. (Load 1 kg, quantity of explosive 20 mm^3, number of experiments in each series 6).
Conditional designations the same as in Fig. 9; 1-8-same as Fig. 9.

Explanation of Results Obtained and Proposed Mechanism of Excitation of Explosion During Blow

The own results German investigators give for their results the following interpretation, which it is expedient to introduce partially even textually. "Consideration of the results obtained leads to the conclusion that sensitivity as a property of explosive in general does not exist or in any case is impossible to establish by tests in small stamping instruments if the requirement of Caste about preventing of lateral extrusion of the explosive are fulfilled."

At good fitting of the piston to the sleeve (gap 0.03 mm) powdery explosives do not display sensitivity. For liquid and gelatinous explosives these conditions correspond to maximum sensitivity.

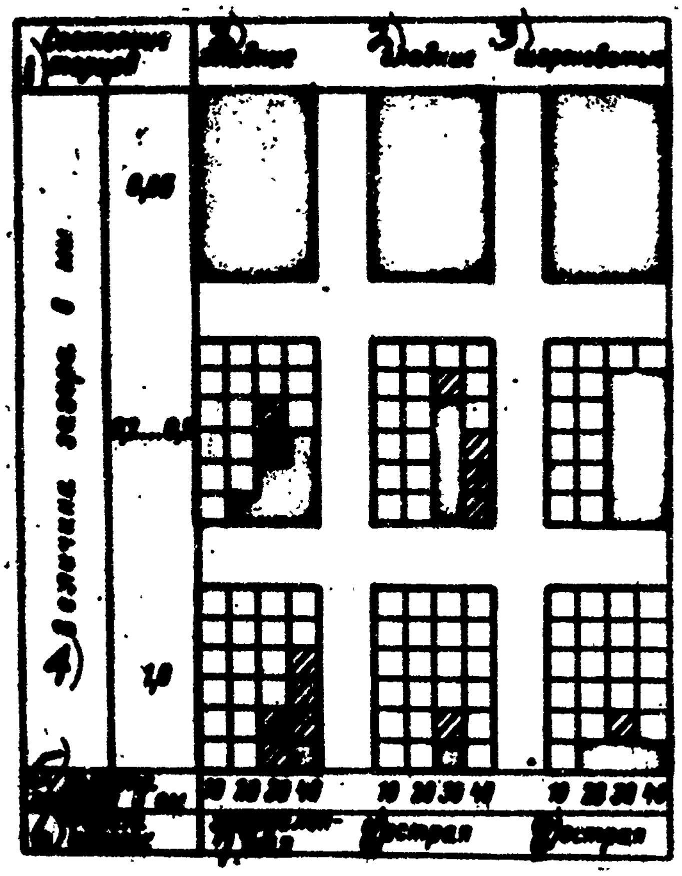

Fig. 13. Sensitivity ammonia gelatin 1 to blow on a drop hammer in Caste instruments, depending upon state of surface of piston faces, the form of their edges, and the magnitude of the gap between them and the sleeve channel. (Load 5 kg, quantity of explosive 60 mm^3, number of experiments in each series 6).
Conditional designations the same as in Fig. 9. 1-8-same as Fig. 9.

Apparently, however, in this case the explosive flows and is detonated at being pressed through with great speed in a narrow gap, inasmuch as explosions occur not between the piston faces but in the gap. If, however, the gap is made larger then speed of extrusion and intensity of influence on the explosive fall so much that explosions are observed only in isolated cases or are quite stopped; this can lead to the false conclusions that such dangerous explosives as nitroglycerine or dynamite are little sensitive to mechanical influences.

Powdery explosives during impact at first are compressed into a tablet and only with great energy of this impact or with a large gap can they be forced into the latter. This pressing the German investigators consider without sufficient foundations, to be stipulated by the presence of air between particles of the explosive which carries along with it explosive during flow after pressure.

On the basis of the fact that with smooth piston faces and the presence on them of loads an increase in the gap from 0.03 to 0.5 mm is weakly reflected on the sensitivity of both nitrocellulose and PETN, one should consider that in these experimental conditions the gap does not play an essential role, since for extruded explosive the volume of the ring, formed by the rounded land is sufficient. One should add that with the exception of very sensitive explosives the main action, about which it is possible to judge by traces of explosion on the piston faces is observed on the periphery of the charge.

Expediency of Development of New Methods

On the basis of the established regularities, the investigators arrived at the correct conclusion on the unfitness of the standard Caste method of testing explosives for sensitivity to impact and of the necessity of developing a new one which would reflect the most dangerous conditions of actions possible to meet during the production and application of explosives. Those last conditions, incidentally, do not correspond to those realised in the standard method, based on effort to exclude the possibility of extrusion and movements in explosives.

In the course of experiments it was observed that the probability of explosion increases in worn-out instruments, leading to the idea of developing a test scheme which would correspond to the conditions of deformation of explosives in such instruments. In connection with this there appeared the test scheme shown in Fig. 14 for test during impact on a film of explosive placed between the faces of two steel free rollers, without directing sleeves, that could hamper the outflow of the explosive.

Inasmuch as certain explosives developed especially high sensitivity to impact between rough surfaces, it was considered expedient to conduct tests also in these conditions. The most suitable for this purpose appeared to be steel plate with notches as by filing.

The diagram of testing explosives on a drop hammer with application of steel plates with notches is shown in Fig. 15. Plates smoothed from below have two rows of notches, whose teeth are at an angle of about 68° to one another, with the distance between them about 0.25 mm; thus there are about 1500 pyramidal points per cm^2. On the plate is placed a batch of the tested explosive, on which a roller with lands along the margin is then set. Actual diameter of the roller end equals 9 mm. On a surface with this diameter there will be nearly 1000 points. A plate is used for 4 experiments and is then replaced.

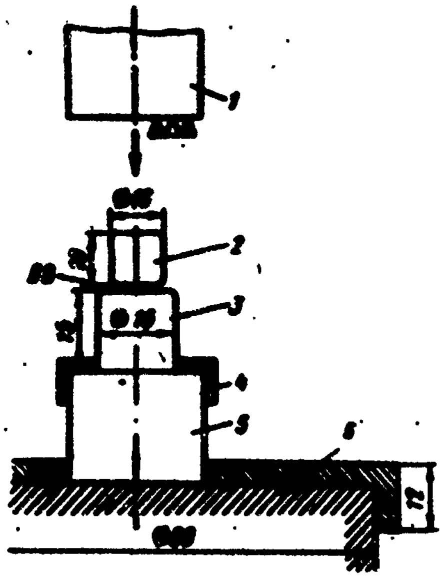

Fig. 14. Scheme for testing explosives on a drop hammer between two free rollers.
1--insert in load (material -- unalloyed steel, containing 1% C, hardness 60 Rockwell -- scale C), 2--upper roller, 3--lower roller, 4--centering ring, 5--anvil, 6--steel block. Material for rollers -- steel 105 Cr 4. Hardness 60--63 Rockwell (scale C). Faces of the rollers are thinly ground and slightly polished.

Usefulness of methods of testing explosives by the schemes shown in Fig. 14 and 15 was checked by investigators on large-crystal PETN (0.1--0.5 mm), whose behavior in the standard instrument was earlier illustrated in Fig. 11. Results of these tests are depicted in Fig. 16. They incidentally confirm the conclusion that explosion appears as a result of flow of the explosive, -- the formation of hot points in Bouden's concept is by itself still insufficient for this --

otherwise during impact through a steel ball (see 2 and 3, Fig. 16) sensitivity would be greater than through a roller, in complete contradiction to that which takes place in reality.

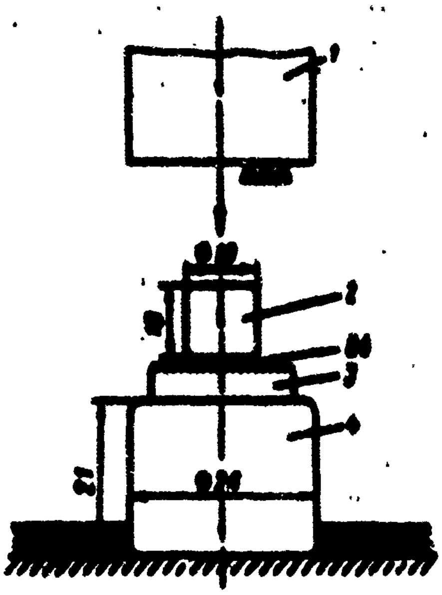

Fig. 15. Scheme for testing explosives on a drop hammer between a free roller and a plate with notches.
1—insert in load (material — alloyed steel, containing 1 % C, hardness 60 Rockwell — scale C), 2—roller (material — steel 105 Cr 4, hardness 60—63 Rockwell — scale C), 3—plate with incision (dimensions 20 x 20 x 5 mm, material — unalloyed steel containing 1.2—1.4% C, hardness 60—63 Rockwell — scale C), 4—anvil (material — steel 105 Cr 4, hardness 60—63 Rockwell — scale C).

In accordance with conditions of the tests the investigators give the following determination of sensitivity. Sensitivity at given definite conditions of experiment is that minimum energy of impact (product of height of fall times weight of load) at which the explosive, during a continuous series of 6 experiments, at least once gives an explosion, i.e., is decomposed completely or partially with an audible, although sometimes very weak, sound.

With this is implied that it is a question of a substance capable of explosion, which should be previously fixed by appropriate methods. This reservation is essential, inasmuch as there are substances which one detonated on the drop hammer, but at the same time are characterised by a very small ability to propagate explosion. Apparently, this is the case with ammonium salts of dinitroorthocresol and bichromate of ammonium.

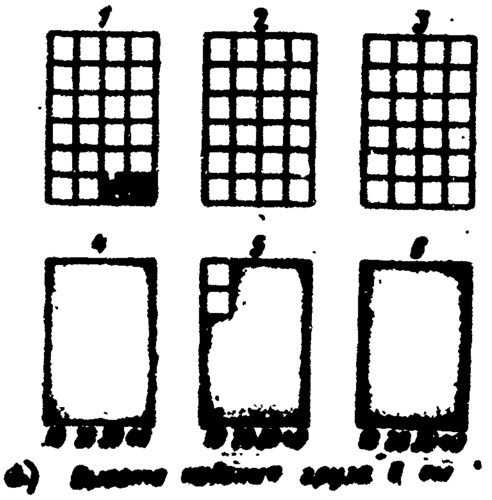

Fig. 16. Sensitivity of PETN (dimensions of particles 0.1—0.5 mm) to impact on copra a drop hammer under different experimental conditions. (Load 5 kg, quantity of explosive 20 mm^3, number of experiments in each series 6).
1—Caste instrument, new, gap 0.03 mm, piston without lands. faces smooth; 2—explosive between a 15 x 15 mm steel roller and a ball 10 mm in diameter; 3—explosive between plate 20 x 20 x 5 mm with notches and a steel ball 10 mm in diameter; 4—often-used Caste instrument with gap of 0.2 to 0.5 mm and rough surface of piston faces; 5—explosive between rollers according to Fig. 14; 6—explosive between plate with notches and a steel roller, according to Fig. 15. Conditional designations the same as in Fig. 9.
a—Height of fall of load in cm.

Second reservation is given textually: "Sensitivity to impact is not a constant of a substance, like density or temperature of melting; moreover, according to our experiments, it depends on different factors".

In the first place, sensitivity is stipulated by the method of test and correspondingly depends on presence of shell, packing, arrangement of test, etc. Secondly, a role is played by the state of the tested explosive, the method of its obtaining, dimensions of particles, and possibly also by climatic conditions during the test. Third, the energy of impact determined as the product of the weight of load and height of fall, is not an absolute characteristic of sensitivity. Observations show that for certain explosives this product, i.e. energy, necessary to obtain explosion, decreases with a decrease of weight of load; apparently, a role is played by sharpness of impact, which increases with an increase in height of fall. The influence of this factor could be excluded by conducting tests at a constant height of fall, but this method has its own draw backs.

Since during impact on an explosive the whole gamut of transitional phenomena from the absence of visible changes in it to full explosion is observed, then for certain determination they are conditionally divided into three categories.

Absence of reaction — signifies absence of decomposition or change of color, burnt odor, sparks, or flame.

Decomposition (change of coloring, partial or full disappearance of explosive without flame), sometimes with weak sparking and without sound, sometimes with a hard metallic sound and with traces of temper coloring.

Explosion (partial or full disappearance of explosive, sound can vary from very weak to very strong. Besides, one can observe flame, escaping from the gap between faces of rollers, and temper coloring on them with dimensions from pinhead size head to covering the whole surface of the face. In special cases a few explosives were ignited without sound. In this case the phenomenon is designated not as decomposition, but as explosion, inasmuch as it embraces the whole test and alternates with explosion; such an explosion is especially designated in the tables below, for example, by an asterisk.

The investigators used the methods they had devised for testing sensitivity of explosives to impact to study a series of explosives. Results of these experiments are listed below.

First Test Method, Intended for Powdery Explosives (Impact on a Charge Located Between Two Rollers Without Sleeves)

Tests were conducted according to the scheme shown in Fig. 14. Batches of explosives were selected by volume and changed within the limits 10—80 mm^3. The most expedient appeared to be a test with 40 mm^3 at a load of 5 kg.

We applied drop hammer of two types - one of the usual Caste type for loads of 1 to 20 kg, and the other for loads of 25 to 1000 g. The results of the experiments are given selectively in Table 2.

For certain explosives, including relatively weak ones (dinitrosopentamethylenetetramine, azide of barium, bichromate of ammonium, etc.), it is possible, by increasing the height of fall, to attain an increase in frequency of explosions up to obtaining them at all 6 experiments;other explosives for example, donarite, tetryl, powder pulp do not give this result; sometimes even a decrease of frequency of explosions with increase in height of fall of load is observed (tetranitrocarbazole).

Certain explosives gave only single explosions (for example, trinitronaphthalene) or explosions only with large heights (for example, azides of alkali earth metals, picric acid). For certain substances decomposition without sound was observed (ammonium nitrate), but others in general did not react to impact (guanidine nitrates, nitroguanidine, dinitro-cresol, trinitrotoluene).

Table 2

(See Table 2 On Following Page)

Table 2

Results of tests of certain explosives for sensitivity to impact blow on a drop hammer between 10 x 10 and 15 x 15 mm steel rollers. (Load 5 kg; quantity of explosive 40 mm^3; number of decompositions (P) and explosions (B) per 6 experiments; dash signifies zero)

1) ВВ	2) Размер частиц *мм*	3) Результат	4) Высота падения груза в *см*								5) Звук взрыва
			10	20	30	40	50	60	80	100	
6) Тэн	0,1—0,5	P B	— 6	— 6							21) От слабого до сильного
7) Калиевая соль гексанитродифениламина	0,1—0,5	P B	— 4	— 5	— 6						22) Слабый
8) Нитроклетчатка 13,4% N	19) Тонковолокнистая	P B	1 3	1 4	1 5	— 6					23) Сильный
9) Натриевая соль динитро-о-крезола	0,1—0,5	P B	— 2*	— 6*	— 6*	— 6*					24) От очень слабого до слабого, частично воспламенение без звука
10) Коллоксилин 12,2% N	19) Тонковолокнистый	P B	1 1	— 5	— 6	— 5	— 6				21) От слабого до сильного
11) Гексоген	0,1—0,5	P B	1 —	1 5	1 5	— 6	1 4	— 3			25) От слабого до средне-сильного
12) Гексанитродифениламин	0,05—0,2	P B	2 —	1 4	1 4	— 4	— 6	— 6	— 6		22) Слабый
13) Донарит 1	20) Крупнозернистый	P B	— —	2 2	2 1	1 1	1 3	1 4	1 1		22) Слабый
14) Тринитрорезорцинат свинца	0,05—0,2	P B		— —	— 1	— 3	— 6	— 6			26) Очень сильный
15) Перхлорат аммония	0,1—0,5	P B		— —	— 1	— 5	— 4	— 6			23) Сильный
16) Пиротехнический состав	0,5—1,0	P B			— —	— 2*	— 4	— 5	— 6		27) От слабого до средне-сильного, в том числе 1 воспламенение без звука *
17) Тетрил	<0,3	P B	— —	1 —	1 —	2 —	1 1	3 1	3 2	2 —	22) Слабый
18) Пикриновая кислота	0,1—2,0	P B	— —	1 —	— —	— —	1 —	1 —	— —	— 2	22) Слабый

Note. With tests of 20 and 60 mm^3 of picric acid analogous results were received.

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* Ignition without sound.

1) Explosive; 2) Dimension of particles, mm; 3) Result; 4) Height of fall of load in cm; 5) Sound of explosion; 6) PETN; 7) Potassium salt of hexanitrodiphenylamine; 8) Nitrocellulose, 13.4% N; 9) Sodium salt of dinitrocresol; 10) Collodion, 12.2% N; 11) Hexogen; 12) Hexanitrodiphenylamine; 13) Donarite 1; 14) Trinitroresorcinate of lead; 15) Perchlorate of ammonium; 16) Pyrotechnic composition; 17) Tetryl; 18) Picric acid; 19) Fine-fibred; 20) Coarse-grained; 21) From weak to strong; 22) Weak; 23) Strong; 24) From very weak to weak, partial ignition without sound; 25) From weak to medium-strong; 26) Very strong; 27) From weak to medium-strong, including 1 ignition without sound *.

Results received with a load of 1 kg for the most sensitive of the explosives given in Table 2 are given in Table 3. Comparison of these tables allows to draw the following conclusions with transition from a load of 5 kg to one of 1 kg the height of fall is increased by less than 5 times; critical energy of impact decreases with an increase in height of fall. A load of 1 kg is not always sufficient for reliable triggering of explosion. Thus, in experiments with pyroxylin in spite of a decrease of quantity of explosive to 10 mm^3 only 50% explosions will be attained and for collodion only single unit explosions are observed. Regular increase in frequency of explosions with height of fall of load is shown by PETN, hexogen, potassium salts of hexanitrodiphenylamine and thermally unstable nitrile of azoisobutyric acid.

Table 3

(See Table 3 On Following Page)

Table 3

Results of tests of certain explosives for sensitivity under impact on a drop hammer between 10 x 10 and 15 x 15 mm steel rollers. (Load 1 kg; quantity of explosive 10 mm^3; number of decompositions (P) and explosions (B) per 6 experiments; dash signifies zero)

1) ВВ	2) Размер частиц мм	3) Результат	4) Высота падения груза в см								5) Звук взрыва
			10	20	30	40	50	60	80	100	
6) Тэн	0,1—0,5	Р	—	—	—	—	—				14) От слабого до сильного
		В	—	2	5	6	6				
7) Калиевая соль гексанитродифениламина	0,1—0,5	Р	—	2	2	1	—	—	3		15) Слабый
		В	—	1	4	2	6	6	3		
8) Гексоген	0,1—0,5	Р		—	—	2	—	—	—	—	16) От слабого до средне-сильного
		В		—	1	1	2	4	4	5	
9) Нитроклетчатка 13,4% N	13) Тонковолокнистая	Р	—	1	1	2	—	1	1	2	17) От очень слабого до слабого, с пробой 40 $мм^3$ сильный звук
		В	—	—	1	1	3	2	1	3	
10) Коллоксилин 12,2% N	13) Тонковолокнистый	Р		—	1	1	3	—	2	1	15) Слабый
		В		—	—	1	—	—	2	—	
11) Натриевая соль динитро-о-крезола	0,1—0,5	Р			—	—	1	2	2	1	18) С пробой 20 $мм^3$ реагирует чаще
		В			—	—	1*	2*	1*	1*	
12) Гексанитродифениламин	0,06—0,2	Р					—	2	1	—	15) Слабый
		В					—	—	3	2	

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*Ignition without sound.

1) Explosive; 2) Dimension of particles, mm; 3) Result; 4) Height of fall of load in cm; 5) Sound of explosion; 6) PETN; 7) Potassium salt of hexanitrodiphenylamine; 8) Hexogen; 9) Nitrocellulose, 13.4% N; 10) Collodion, 12.2% N; 11) Sodium salt of dinitro-cresol; 12) Hexanitrodiphenylamine; 13) Fine-fibred; 14) From weak to strong; 15) Weak; 16) From weak to medium-strong; 17) From very weak to weak — with test of 40 mm^3 strong sound; 18) With test of 20 mm^3 reacts more frequently.

The investigators explain results of tests of different explosives on a drop-hammer on the basis of the following considerations.

Under action of impact of falling load, after achievement of definite pressure, the tested powdery explosive starts to be forced between the faces with significant speed, which plays an essential role in triggering explosion. If possibility of extrusion is absent, then sensitivity is strongly decreased.

For a powdery explosive under the described test conditions influence is sufficient for friction during flow, breaking of crystals etc. to cause explosion; liquid and gelatinous explosives due to their high fluidity, require more severe conditions of flow.

Fig. 17. Crown of deep notches on faces of steel rollers after explosion of tetryl. (Load 5 kg, height of fall 60 cm, quantity of explosive 40 mm^3; test in instrument assembled according to diagram in Fig. 14).

On the left is the face of the lower roller, on the right that of the upper.

Such an explanation is favored, in particular, by observations made during experiments with tetryl, which is usually more frequently decomposed without than with explosion with smooth faces. At removal by acetone of residue of the explosive on periphery there was detected a series of deep radial notches, which were located on both the lower and the upper rollers and looked as if they had been burned by a microburner (Fig. 17). Since other phenomena, including weak temper coloring, were not detected nearby, one can consider that these notches on the faces of the rollers appeared as a result of local explosions with high-temperature products.

The fact that notches appear only on periphery, in narrow ring-shaped zone about 0.5 mm in width, indicates that only here appear conditions for explosion. Apparently, the radial direction of notches is connected with the radial flow of particles of the explosive. The triggering of explosion on the periphery of the faces is also supported by the location of temper coloring which is frequently limited to the peripheral zone.

As a matter of fact, triggering of explosion under impact has many of the general characteristics of triggering during friction; the latter, possibly, is a necessary condition for triggering of explosion under impact.

Second Test Method, Intended for Liquid and Gelatinous Explosives (Impact on Charge Located Between Two Rollers With Sleeves)

Liquid and gelatinous explosives are not detonated in tests by the first method. Sufficienty high frequency of explosions, corresponding to their danger in handling, are obtained for liquid explosives in worn-out stamping instruments with rough piston faces or in instruments with smooth faces (with or without lands), but with small gaps present in the sleeve. These conditions are more definite, and therefore it is recommended that testing of liquid explosives be oriented on them. Diameter of rollers was taken equal to 10 mm, the thickness of sleeve to 3 mm, height to 13 mm and gap (difference of diameters) no more than 15 microns. Data obtained in test of nitroglycerine and nitroglycol by this method are given in Table 4.

Table 4

Tests of liquid explosives for sensitivity to impact on a drop hammer between 10 x 10 mm rollers with rounded lands in the presence of a sleeve. (Load 0.1 kg; volume of tested explosive 10 mm^3; number of explosions is given from 6 experiments)

1) ВВ	2) Высота падения в см							
	10	20	30	40	50	60	80	100
3) Нитроглицерин	0	0	1	5	6	6		
4) Нитрогликоль				0	2	3	3	6

Note. Sound of explosion very strong.
1) Explosive; 2) Height of fall in cm; 3) Nitroglycerine; 4) Nitroglycol

Third Method of Test of Sensitivity of Explosive (on Plates with Notches)

Tests were conducted according to the scheme shown in Fig. 15. Their results are given in Tables 5 and 6. Data in Tables 5 and 6 show large sensitivity of the test method used. This sensitivity appears as a fast increase in the frequency of explosions. Advantages of method are shown not only in tests of high-sensitivity explosives. Thus, while picric acid between rollers is detonated in separate cases only with a 100-cm height of fall of load, on a plate with notches it regularly gives weak explosions with the same load (5 kg) starting from a height of 20 cm. And with this method an increase in frequency of explosions is observed in the case of a decrease in weight of load at a given energy of impact.

An advantage of the method of testing explosives on plates with notches is the possibility, with a load not exceeding 20 kg, to determine the sensitivity of even such little-sensitive explosives as dinitrobenzene, which cannot be done on roller instruments.

The great ease of appearance of explosion on plate with notches to as compared to that on rollers is explained by great restriction in this case of the radial flow of the explosive. Characteristics of this flow during explosion are detected by the location and direction of the usual carbonized residues and by the temper coloring on the surface of the upper roller face , which frequently start from imprints of the notch ridges and are directed along the channels or radially.

It is natural to assume that at the points of contact of notch ridges and the roller face heatups will appear as a result of conversion of deformation energy into heat. These heatups, in combination with destruction of crystals during impact and processes of flow of explosive in the grooves, cause explosion.

The high sensitivity of the considered method of testing explosives is stipulated by the fact that impact energy is distributed here nonuniformly. Besides, in grooves of plate there remains more explosive, than on the face of flat rollers.

General Characteristic of Sensitivity of Different Explosives According to Various Methods of Test

Comparison of the data obtained during tests on plates and in roller instruments are presented in Table 7.

By data from the tests conducted, and first of all from tests on plates with notches, the investigators divided the studied substances into groups by sensitivity in the following manner:

1 group : not sensitive to impact(with a load of 5 kg in the given test conditions neither decomposition, nor explosion is observed);

2 group: little sensitive (with a load of 5 or 1 kg only decomposition is observed);

3 group: sensitive to impact (with a load of 5 or 1 kg explosions are observed which do not occur with a weight of 0.1 kg or less).

With this, in accordance with the experimental data in hand, it is possible further to subdivide explosives of group 3 into the following subgroups:

a) conditionally sensitive to impact -- single explosions;

b) sensitive to impact, but frequency does not increase to 100% or explosions occur irregularly;

c) normally sensitive to impact in the sense that probability of explosion is steady and increases more or less fast from 0 to explosions in all 6 experiments.

Table 5

Results of tests of certain explosives for sensitivity to impact on a drop hammer with use of plates with notches (Load 5 kg; quantity of explosive 40 mm^3; number of decompositions (P) and explosions (B) per 6 experiments; dash signifies zero)

1) ВВ	Размер частиц, мм 2)	Обозначение результата 3)	4) Высота падения в см								Звук при взрыве 5)	Примечание 6)
			10	20	30	40	50	60	80	100		
7) Калиевая соль гексанитродифениламина	0,1—0,5	P B	— 6	— 6							15) Сильный	
8) Натриевая соль динитро-о-крезола	0,1—0,5	P B	— 4*	— 6	— 6						16) От слабого до среднесильного, в том числе одно воспламенение без звука	
9) Гексанитродифениламин	0,06—0,2	P B	3 3	— 6	— 6						17) От слабого до среднесильного	
10) Хлоратит 1	14) Тонкозернистый	P B	— 3	— 5	— 6						18) От среднесильного до сильного	
11) Тринитрорезорцин	0,1—0,5	P B	2 2	— 4	— 5	1 3	2 4	— 6			17) От слабого до среднесильного	
12) Тетрил	<0,3	P B	— 3	2 4	4 2	2 4	1 5	— 6	— 6	— 6	19) От очень слабого до слабого	
13) Нитрил азоизомасляной кислоты	0,1—0,2	P B	— 2	— 1	1 —	— 1	1 —	2 —	— —	— —	20) То же	21) При пробе 10 $мм^3$ число взрывов возрастает до 6

1) Explosive; 2) Dimension of particles, mm; 3) Designation of result; 4) Height of fall in cm; 5) Sound during explosion; 6) Note; 7) Potassium salt of hexanitrodiphenylamine; 8) Sodium salt of dinitro-cresol, 9) Hexanitrodiphenylamine; 10) Chloratite 1; 11) Trinitroresorcin; 12) Tetryl; 13) Nitrile of azoisobutyric acid; 14) Fine-grained; 15) Strong; 16) From weak to average-strong, including one ignition without sound; 17) From weak to average-strong; 18) From average-strong to strong; 19) From very weak to weak; 20) The same; 21) In tests with 10 mm^3 the number of explosions increases to 6.

Table 5 (Cont'd)

22) Бихромат аммония	0,1—0,5	Р В	1 —	— 4	— 6	— 6					От слабого до сильного 34)	
23) Динитрозопентаметилентетрамин	0,06÷0,3	Р В	1 —	1 3	— 6	— 6	— 6				Сильный 35)	
24) Перхлоратаммония	0,1÷0,5	Р В	— —	1 3	— 5	— 6	— 6				Сильный 35)	
25) Черный порох (мякоть)	<0,5	Р В	— —	— 2	— 4	— 6	— 6				От сильного до очень сильного 36)	
26) Пикриновая кислота	0,1÷2,0	Р В	1 —	1 2	— 2	— 6	— 6	— 6	— 6		Слабый 35)	
27) Тринитробензойная кислота	<0,2	Р В	2 —	— 4	2 4	1 4	2 4	2 3	2 4	4 2	34) От слабого до сильного	40) При пробах 10 и 20 мм³ число взрывов возрастает до 6
28) Тетранитрокарбазол	0,1÷0,5	Р В	1 —	1 2	— 5	— 5	1 2	— 4	4 2		37) От слабого до среднесильного	
29) Аммонжелат 3	Гель из крупных частиц 33)	Р В	1 —	3 2	1 5	— 4	2 2	2 3	1 3	— 2	35) Слабый	41) При пробах 10 и 20 мм³ больше взрывов
30) Этилендиаминдинитрат	0,1÷0,5	Р В	1 —	1 2	4 1	2 4	— 4	2 3	2 4		38) От очень слабого до слабого	42) При пробах 10 и 20 мм³ число взрывов возрастает до 6
31) Азид бария	0,1÷0,5	Р В		— —	1 4	— 4	— 6	— 5	—		39) От среднесильного до очень сильного	
32) Тринитронафталин	0,1÷0,5	Р В	— —	3 —	— 4	— 5	— 4	— 6			34) От слабого до сильного	

22) Bichromate of ammonium; 23) Dinitrosopentamethylenetetramine; 24) Perchlorate of ammonia; 25) Black powder (meat); 26) Picric acid; 27) Trinitrobenzoic acid; 28) Tetranitrocarbazole; 29) Ammonia gelatin 3; 30) Ethylenediamine dinitrate; 31) Barium azide; 32) Trinitronaphthalene; 33) Gel from large particles; 34) From weak to strong; 35) Strong; 36) From strong to very strong: 37) From weak to average-strong; 38) From very weak to weak; 39) From average-strong to very strong; 40) In tests with 10 and 20 mm³ the number of explosions increases to 6; 41) In tests with 10 and 20 mm³ there are more explosions.

Table 5 (Cont'd)

1 ВВ	Размер частиц мм 2	Обозначение результата 3	4 Высота падения в см								Звук при взрыве 5	6 Примечание
			10	20	30	40	50	60	80	100		
7 Аммониевая соль динитро-о-крезола	<0,2	Р		—	—	—	—	—	1	—	15 От слабого до среднесильного	
		В		—	3	3	6	6	5	6		
8 Пиротехнический состав	0,5—1,0	Р		—	—	1	—	—	—		16 От сильного до очень сильного; в том числе 1 воспламенение без звука	
		В		—	1	3	5*	4	4			
9 Оксицианид ртути	0,1—0,5	Р		—	—	—	1	—	—		17 От сильного до очень сильного	
		В		—	1	1	1	5	6			
10 Донарит 1	14 Зернистый	Р	—	2	—	—	2	—	1		18 Слабый	21 При пробе 10 мм³ от высоты 10 см число взрывов возрастает до 5
		В	—	—	1	2	1	2	—			
11 Натриевая соль п-нитрофенола (безводная)	0,06—0,2	Р		—	1	2	—	1	—	—	15 От слабого до среднесильного	
		В		—	—	3	4	3	5	5		
12 Азид стронция	0,1—0,5	Р		—	—	—	—	—	3	1	19 От сильного до очень сильного; частично воспламенение без звука	При пробе 5 мм³ от высоты 10 см число взрывов возрастает до 6 22
		В		—	—	1*	2*	2*	3*	5*		
13 Азид кальция	0,1—0,5	Р		—	—	—	—	—	1	—	20 Сильный	При пробе 5 мм³ от высоты 20 см число взрывов возрастает до 6 23
		В		—	—	1*	1*	—	2	2		

1) Explosive; 2) Dimension of particles, mm; 3) Designation of result; 4) Height of fall in cm; 5) Sound during explosion; 6) Note; 7) Ammonium salt of dinitro-cresol; 8) Pyrotechnic composition; 9) Oxycyanide of mercury; 10) Donarite 1; 11) Sodium salt of n-nitrophenol (anhydrous); 12) Azide of strontium; 13) Azide of potassium; 14) Granular; 15) From weak to average-strong; 16) From strong to very strong, includes 1 ignition without sound; 17) From strong to very strong; 18) Weak; 19) From strong to very strong; partial ignition without sound; 20) Strong; 21) In test with 10 mm³ from a height of 10 cm number of explosions increases to 6; 22) In test with 5 mm³ from a height of 10 cm number of explosions increases to 6; 23) In test with 5 mm³ from height of 20 cm number of explosions increases to 6.

Table 5 (Cont'd)

1	Тринитроанилин	0,1—0,5	Р В				— —	— 1	— —	2 —	3 —	Слабый 8	Отдельные взрывы 9
2	Оксалат серебра	<0,2	Р В		— —	— —	— —	— —	— —	— 1	1 1	Слабый 8	При пробе 60 мм³ от высоты 40 см число взрывов возрастает до 6 10
3	Тринитротолуол	<0,2	Р В		— —	3 —	5 —	6 —	6 —	4 —	6 —		
4	Гуанидиннитрат	0,1÷0,5	Р В				— —	— —	— —	— —	— —		
5	Динитробензол	7 Призмы 0,01—0,2	Р В				— —	— —	— —	— —	— —		
6	Динитро-о-крезол	<0,2	Р В				— —	— —	— —	— —	— —		

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*Ignition without sound. (See page 168)

1) Trinitroaniline; 2) Oxalate of silver; 3) Trinitrotoluene; 4) Guanidine nitrate; 5) Dinitrobenzene. 6) Dinitro-cresol; 7) Prism; 8) Weak; 9) Separate explosions; 10) In test with 60 mm^3 from a height of 40 cm number of explosions increases to 6.

Table 6

Results of tests of certain explosives for sensitivity to impact on a drop hammer with use of plates with notches (Load 1 kg, quantity of explosive 5 mm^3, number of experiments 6, conditional designations the same as in Table 5)

1 ВВ	2 Размеры частиц *мм*	3 Обозначение результата	4 Высота падения в *см*								5 Звук при взрыве
			10	20	30	40	50	60	80	100	
6 Смесь хлората калия с красным фосфором 75/25	0,06—0,075	Р В	— 6	— 6							14 Очень сильный
7 Ацетиленистое серебро с примесью азотнокислого серебра (из HNO$_3$-раствора)	<0,001	Р В	— 6	— 5							15 Сильный
8 Ацетиленистая ртуть	13 Тонкозернистая	Р В	— 4	— 6	— 6						16 От слабого до среднесильного
9 Циануртриазид	0,02—0,55	Р В	— 3	— 6	— 6						15 Сильный
10 Ацетиленистое серебро (из нейтрального раствора)		Р В	— 2	— 5							16 От слабого до среднесильного
11 Ацетиленистое серебро (из NH$_3$-раствора)	0,01	Р В	— 2*	— 5*	— 6*						17 Слабая вспышка
12 Азид свинца	0,01—0,1	Р В	— 2	— 4	— 4	— 6	— 6				14 Очень сильный

1) Explosive; 2) Dimensions of particles, mm; 3) Designation of result; 4) Height of fall in cm; 5) Sound during explosion; 6) Mixture of chlorate of potassium with red phosphorus, 75/25; 7) Silver acetylide with impurity of silver nitrate (from HNO$_3$ solution); 8) Mercury acetylide; 9) Cyanurtriazide; 10) Silver acetylide (from neutral solution); 11) Silver acetylide (from NH$_3$ solution); 12) Azide of lead; 13) Fine-grained; 14) Very strong; 15) Strong; 16) From weak to average-strong; 17) Weak flash.

*Ignition without sound

Table 6 (cont'd)

1	Ацетиленистая медь		Р В	— 2*	— 3*	— 6*	— 6*	— 6*				13 Слабый, вещество частично воспламеняется без звука, обильное выделение сажи
2	Перекись трициклоацетона	<0,07	Р В	— 1	— 3	— 5	— 6	— 6				14 Сильный
3	Азид ртути (I)	12 Зернистый	Р В	— 2	— 2	— 4	— 6	— 6				15 Очень сильный
4	Гексаметилентрипероксиддиамин	0,1	Р В	— 1	— 3	— 2	— 3	— 6	— 6			15 Очень сильный
5	Тринитрорезорцинат свинца	0,06—0,2	Р В	— —	— 5	— 3	— 2	— 6	— 6			15 Очень сильный
6	Гремучая ртуть белая	0,06—0,8	Р В	— —	— 3	— 5	— 5	— 5	— 4	— 6		15 Очень сильный
7	Тетразен	0,003—0,1	Р В	— —	— 2	— 5	— 4	— 6	— 6			14 Сильный
8	Гремучая ртуть серая	0,06—0,8	Р В	— —	— 2	— 4	— 4	— 4	— 2	— 6		15 Очень сильный
9	Щавелевокислая ртуть	0,06—0,5	Р В		— —	— 4	— 4	— 6	— 6			16 Слабый
10	Эритриттетранитрат	0,1—0,5	Р В					— —	— —	— 2	— 2	15 Очень сильный
11	Тэн	0,1—0,5	Р В					— —	— —	— 2	— 1	14 Сильный

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*Ignition without sound.

1) Cuprous acetylide; 2) Peroxide of tricycloacetone; 3) Azide of mercury (I); 4) Hexamethylenetriperoxide diamine; 5) Trinitroresorcinate of lead; 6) Mercury fulminate, white; 7) Tetrazene; 8) Mercury fulminate, gray; 9) Oxalic acid mercury; 10) Erythrytetetranitrate; 11) PETN, 12) Granular; 13) Weak, substance is partially ignited without sound, abundant separation of soot; 14) Strong; 15) Very strong. 16) Weak

4 group: very sensitive to impact (explosions occur even at a load of 0.1 kg or less with regular increase in frequency).

This division is conditional, but it gives the possibility to be oriented in a practical appraisal of the danger of explosives.

According to data from tests on plates with notches, explosives can be classified as follows:

group 1 -- guanidine nitrate, dinitro derivative benzene, dinitrocresol;

group 2 -- trinitrotoluene;

group 3 --a) trinitroaniline;

3 b) ammonia gelatin 3, tetranitrocarbazole, pyrotechnic composition based on nitrate of barium, iron filings and aluminum, n-nitrophenolate of sodium.

3 c) nitric acid ester of cellulose tissue--pyroxylin and collodion; hexanitrodiphenylamine and its potassium salt; perchlorate and bichromate of ammonium; azide of alkali earth metals; trinitro compounds of phenol, resorcin, benzoic acid, and naphthalene; sodium and ammonium salts of dinitrocresol; chloratite 1 and donarite 1; gas generating substances -- dinitrosopentamethylenetetramine and nitrile of azoisobutyric acid; tetryl; ethylendiamine dinitrate, oxycyanide of mercury; oxalate of silver; hexogen.

group 4 -- armstrong mixture ($KClO_3$ and red phosphorus, 75/25), organic peroxides -- hexamethylenetriperoxidediamine and peroxide of tricycloacetone; cyanurtriazide; salts of heavy metals of hydrazoic acid (Pb, Hg), fulminic acid (Hg), styphnic acid (Pb), oxalic acid (Hg) and acetylene (Ag, Hg, Cu); tetrazene and nitric-acid esters -- erythritetetranitrate and pentaerythrite tetranitrate.

Table 7

Sensitivity of explosives, determined between two steel rollers and on plates with notches, expressed as minimum energy of impact at which explosions are observed

(6 parallel experiments; arrangement of explosives in order of decrease of sensitivity on plates with notches)

1 Взрывчатое вещество	2 Размер частиц ВВ *мм*	3 Минимальная энергия удара в *кГ·м*						
		4 между стальными роликами по схеме фиг. 14			5 на пластинках с насечкой по схеме фиг. 15			
		6 Вес груза в *кг*						
		5	1	0,1	5	1	0,1	0,025
7 Смесь хлората калия с красным фосфором 75/25	0,06—0,075			0,003				0,003
8 Ацетиленистое серебро с примесью азотно-кислого серебра (из HNO_3-раствора)	0,001	1	0,5					0,003
9 Ацетиленистая ртуть	12 Тонкозернистая			0,06				0,003
10 Циануртриазид	0,02—0,55			0,04				0,003
11 Ацетиленистое серебро (из нейтрального раствора)		1	0,2					0,003

1) Explosive; 2) Dimension of explosive particles, mm; 3) Minimum energy of impact in kG · m; 4) between steel rollers according to scheme of Fig. 14; 5) on plates with notches according to scheme of Fig. 15; 6) Weight of load in kg; 7) Mixture of chlorate of potassium with red phosphorus, 75/25; 8) Silver acetylide with impurity of nitric-acid silver (from HNO_3-solution); 9) Acetylide of mercury; 10) Cyanurtriazide; 11) Silver acetylide (from neutral solution); 12) Fine-grained.

Table 7 (continued)

1 Взрывчатое вещество	2 Размер частиц ВВ мм	3 Минимальная энергия удара в кГ·м						
		4 между стальными роликами по схеме фиг. 14			5 на пластинках с насечкой по схеме фиг. 15			
		6 Вес груза в кг						
		5	1	0,1	5	1	0,1	0,025
7 Ацетиленистое серебро (из NH_3-раствора)	0,01		0,1	0,08				0,003
8 Азид свинца	0,01—0,1							0,008
9 Ацетиленистая медь								0,003
10 Перекись трициклоацетона	0,07			0,01				0,003
11 Азид ртути HgN_3	27 Зернистый			0,03				0,003
12 Гексаметилентрипероксиддиамин	0,1			0,01				0,003
13 Тринитрорезорцинат свинца	0,05—0,2	1,5						0,005
14 Гремучая ртуть белая	0,05—0,8							0,005
15 Тетразен	0,003—0,1	1	0,6					0,006
16 Гремучая ртуть серая	0,05—0,8			0,06				0,006
17 Щавелевокислая ртуть	0,06—0,5	3					0,02	0,008
18 Эритриттетранитрат	0,1—0,5	0,5	0,2				0,08	0,02
19 Тэн	0,1—0,5	0,5	0,2				0,06	0,02
20 Нитрил азоизомасляной кислоты	0,1—0,2	0,5	0,2		0,5	0,2		
21 Хлоратит 1**	28 Тонкозернистый				0,5	0,2		
22 Тетрил	0,3	2,5	0,5		0,5	0,2		
23 Нитроклетчатка 13,4% N	29 Тонковолокнистая	0,5	0,3			0,2		
24 Коллоксилин 12,2% N	30 Тонковолокнистый	0,5	0,4		1	0,2		
25 Калиевая соль гексанитродифениламина	0,1—0,5	0,5	0,2		0,5	0,3		
26 Аммонит 1***	31 Желатинообразный		0,1*		0,5	0,4		

1-6) same as pp 173; 7) Silver acetylide (from NH_3 - solution); 8) Azide of lead; 9) Cuprous acetylide; 10) Peroxide of tricycloacetone; 11) Azide of mercury HgN_3; 12) Hexamethylenetriperoxidediamine; 13) Trinitroresorcinate of lead; 14) Mercury fulminate, white; 15) Tetrazene; 16) Mercury fulminate, gray; 17) Oxalic acid mercury; 18) Erythritetetranitrate; 19) PETN; 20) Nitrile azoisobutyric acid; 21) Chloratite 1**; 22) Tetryl; 23) Nitrocellulose, 13.4% N; 24) Collodion, 12.2% N; 25) Potassium salt of hexanitrodiphenylamine; 26) Ammonia 1***; 27) Granular; 28) Fine-grained; 29) Fine-fibred; 30) Fine-fine-fibred; 31) Gelatinous.

Table 7 (continued)

1 Взрывчатое вещество	2 Размер частиц ВВ мм	3 Минимальная энергия удара в кГ·м						
		4 между стальными роликами по схеме фиг. 14			5 на пластинках с насечкой по схеме фиг. 15			
		6 Вес груза в кг						
		5	1	0,1	5	1	0,1	0,025
7 Аммонжелит 3 ****	30 Желатинообразный				1	0,4		
8 Гексоген	0,1—0,5	1	0,3			0,4	0,1	
9 Тринитробензойная кислота	0,2	1			1	0,4		
10 Донарит *****	31 Тонкозернистый	1	0,6		1,5	0,4		
11 Динитроортокрезолят натрия	0,1—0,5	0,5	0,5		0,5	0,4		
12 Нитроглицерин				0,03*	0,5	0,5		
13 Тринитрорезорцин	0,1—0,5	1			0,5	0,5		
14 Гексанитродифениламин	0,06—0,2	1	0,8		0,5	0,5		
15 Нитрогликоль				0,05*	1	0,5		
16 Пикриновая кислота	0,1—2,0	5			1	0,5		
17 Азид кальция	0,1—0,5	5			2	0,6		
18 Азид стронция	0,1—0,5	3			2	0,6		
19 Азид бария	0,1—0,5	1			1,5	0,8		
20 Бихромат аммония	0,1—0,5	1,5			1	0,8		
21 Пороховая мякоть (75% KNO_3)	0,5	1,5			1	1		
22 Динитрозопентаметилентетрамин	0,06—0,3	1			1			
23 Перхлорат аммония	0,1—0,5	1,5			1			
24 Тетранитрокарбазол	0,1—0,5	1			1			
25 Этилендиаминдинитрат	0,1—0,5	1,5			1			
26 Тринитронафталин	0,1—0,5	1,5			1,5			
27 Динитроортокрезолят аммония	0,2	1,5			1,5			
28 Пиротехнический состав ******	0,5—1,0	2			1,5			
29 Оксицианид ртути	0,1—0,5	2			1,5			

1-6) same as pp 173; 7) Ammonshelit 3****; 8) Hexogen; 9) Trinitrobenzoic acid; 10) Donarite *****; 11) Dinitroorthocresolate of sodium; 12) Nitroglycerine; 13) Trinitroresorcin; 14) Hexanitrodipheynlamine; 15) Nitroglycol; 16) Picric acid; 17) Aside of calcium; 18) Aside of strontium; 19) Aside of barium; 20) Bichromate of ammonium; 21) Powder pulp (75% KNO_3); 22) Dinitrosopentamethylenetetramine; 23) Perchlorate of ammonium; 24) Tetranitrocarbasole; 25) Ethylenediaminedinitrate; 26) Trinitronaphthalene; 27) Dinitroorthocresolate of ammonium; 28) Pyrotechnic composition******; 29) Oxycyanide of mercury; 30) Gelatinous; 31) Fine-grained.

Table 7 (continued)

1 Взрывчатое вещество	2 Размер частиц ВВ мм	3 Минимальная энергия удара в кГ·м						
		4 между стальными роликами по схеме фиг.14			5 на пластинках с насеч-кой по схеме фиг. 15			
		6 Вес груза в кг						
		5	1	0,1	5	1	0,1	0,025
7 Паранитрофенолят натрия (безводный)	0,06—0,2	2			2			
8 Тринитроанилин	0,1—0,5				2,5			
9 Щавелевокислое серебро	0,2	5			4			

1-6) same as pp 173; 7) paranitrophenolate of sodium (anhydrous); 8) Trinitroaniline; 9) Oxalic acid silver

*Values were obtained between 10 x 10 mm steel rollers located in a sleeve.

** Chloratite 1 consists of $KClO_3$ (88.5%), wood flour (8.5%), and paraffin oil (3%).

***Ammonia gelatin 1 consists of ammonium nitrate (52.3%), nitroglycol (37.7%), trinitrotoluene (4%), collodional cotton (1.8%), wood flour (4%), and Prussian red (0.2%).

****Ammonium gelatin 3 contains ammonium nitrate (55%), diglycoldinitrate (22%), trinitrotoluene (5%), dinitrotoluene (6%), and other components.

*****Donarite 1 contains ammonium nitrate (80%), aromatic nitro compounds (14%), nitroglycerine (4%), and other components.

******Pyrotechnic composition contains nitrate of barium (52%), iron filings (30%), dextrin (9%), Al (7%), and other components.

In conclusion the investigators underline the value as a factor of triggering of explosion of narrow slots, through which explosives especially liquid or gelatinous, are pressed. Such phenomena can take place during pressing in pressure cast molds, during mixing in mixers, if the wings of mixer approach too near the walls, in machines for gelatinous explosives, etc.

Another essential factor in the triggering of explosion during impact is the possibility of extrusion of the substance, as is also the state of the impacting surfaces (smooth or rough).

Conclusion

The considered experimental data and considerations of foreign investigators basically are in agreement with the results of the work of N. A. Kholevo, done by him and partially published significantly earlier. This includes the dependence of sensitivity on the possibility of flow of the explosive during impact on a drop hammer(presence and magnitude of gaps), on the ability of the explosive to flow (distinction between powdery explosives on the one hand and liquid and gelatinous on the other), the optionality of parallelism between frequency of explosions and height of fall of load, etc. Moreover, N. A. Kholevo in his own conclusions advanced significantly further than, for example, the German investigators. He not only ascertained the variability of sensitivity (frequency of explosions) under different conditions, but also gave a well-grounded explanation[1] of the influence of these conditions.

New in the work of the German invectigators is the proposal of the third method, (besides instruments No. 1 and 2 in German modification) i.e., to apply the test by impact on plates with notches, with which sensitivity of many explosives appears much higher than with other methods. In essence this is not surprising, since in the method of plates with notches, the impact, owing to the complexity of the outflow of the explosion creates increased pressure, and besides, contact of the notch ridges with plane of roller can lead to local heatups. Similar heat ups were obtained by Bouden [1] by impact on a needle placed on the anvil; he measured the temperature appearing in this case and showed that easily-burning explosives, like cynurtriazide, can be detonated in this way.

To trigger burning of difficult-burning explosives one needs, besides heatup, high pressure, which is created during experiments on plates with notches. Besides, as distinguished from experiments with two rollers, heatup appears while the layer of explosive between the plate and the roller still has sufficient thickness so that burning can be propagated in it, this is not always assured in tests of low-viscosity explosives between two rollers.

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[1] See present collection, page 5.

Positive side of test on plates with notches consists also in the fact that local heatup is created in known measure independently of properties (fluidity) of the explosive and, if it is able to burn, then this ability can be developed. In essence, impact on an explosive on plates with notches is a test on inflammability, although the latter is established in the given case under somewhat indefinite conditions.

When we conduct tests in instruments No. 1 and 2, in order to receive explosion we must not only ensure the possibility of its propagation, but also create the conditions for triggering this explosion. Absence of the latter leads to refusals. For example, aside of lead in instruments No. 1 and 2 do not give explosions for this reason, or nitroglycerine or trotyl in instrument No. 2.

Bearing these considerations in mind, one should recognise that testing on plates with notches is useful in the sense that if it gives a negative result, then this is proof of the low inflammability of the tested explosive.

The results of Ljungberg's experiments are interesting, inasmuch as they show that change of stress in time under impact, taken by N. A. Kholevo, without direct experimental proofs, exists in reality.

The reader may ask, if these foreign authors basically repeated paths already taken by N. A. Kholevo, whether it is necessary for us to consider these works.

Such consideration is expedient, in particular, because the works of N. A. Kholevo, owing to the great originality of his presentations, were not in good time properly evaluated by many investigators and did not receive that development and use that they merit. In connection with the circumstance that foreign investigators, in order to obtain an objective concept of the sensitivity of explosives, came upon the same path followed by N. A. Kholevo and arrived at certain of his conclusions which it would be useful to know to a wide circle of persons conducting work with explosives and especially to these investigators who till now could not in the proper measure understand and estimate the value of the works of N. A. Kholevo to the science of explosion and the support of safety during work with explosives.

Side by side with this, the investigations considered contain much actual material on the sensitivity of a large number of explosives under various test conditions and thus offer significant value not only as confirmation of many conclusions of N. A. Kholevo, but also in themselves.

Results

Investigations of American, Swedish and German investigators on the sensitivity of explosives to impact led them to a conclusion on the strong changeability of sensitivity, depending upon test conditions and the physicomechanical properties of the explosive. The usual tests on a drop hammer in Caste stamping instruments, as well as any other similar test, cannot, taken alone, give a full characterisation of the danger of explosives in handling. Therefore in the selection of the test method it is necessary to take into account the physical properties of the substance and the character those influences, in reference to that which one is required to establish the degree of its danger.

New variants are recommended of tests of explosives for sensitivity to impact -- tests between two rollers without a sleeve for powdery (distinctly viscous) explosives (analogous to instrument No. 2 of N. A. Kholevo), between two rollers with a sleeve with a small gap for liquid and gelatinous explosives (analogous to instrument No. 1 of N. A. Kholevo) and between a roller and a plate with notches, useful for explosives of diverse physical structure.

The results and conclusions of foreign investigators, the most part repeat and thus confirm those data and conclusions reached much earlier by N. A. Kholevo in the Kazan' Chemcial-Technological Institute.

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Article No. 9 Part 1

Pages 131-143

II. THERMAL DECOMPOSITION OF EXPLOSIVES

K. K. Andreyev and G. N. Bespalov

9. On the Influence of Water On the Decomposition of Nitroglycerine At Increased Temperatures

In a number of articles [1], [2], [5], [12], [13] the main characteristics of thermal disintegration of nitroglycerine (NG) are established. In vapors (130-150°) decomposition occurs with a speed, proportional to their pressure, and diminishes in time according to a law, close to the law of reaction of the first order. In the presence of a liquid phase, the speed of gas formation in that same range of temperatures is less, moderately increases in time and slightly depends on the pressure of the products of disintegration.

If, however, during decomposition a certain critical pressure of products of disintegration is reached, then the speed of gas formation begins quickly, approximately proportional to the square of pressure, increases and can attain very large values, one hundred and a thousand times exceeding its initial value. "Critical" pressure constitutes nearly 200 mm Hg at 100°. It is not strictly constant: in early stages of disintegration, "critical" pressure is greater; one of the possible causes of this can be the change in composition of the products of decomposition due to its flow; "critical" pressure is increased with the increase of temperature, obviously due to the influence of the latter on the solubility of gases in a liquid.

The onset of sharp acceleration of gas formation after achievement of "critical" pressure is explained, in accordance with the main thought of S. Z. Roginskiy [5], [13], by the fact that pressure determines the concentration of gaseous products of disintegration in liquid NG. Apparently, these products - acids and water - lead to fast development of hydrolytic and subsequent oxidising-reduction reactions, the speed of which is much greater, than the speed of initial thermal disintagration. If decomposition is conducted at large degrees of filling of the reaction vessel, when the gaseous products of disintegration almost wholly remain in the liquid, then sharp acceleration of decomposition occurs at 100° approximately after 9 hours. At 60° this time is increased to 550 hours. The degree of disintegration, with which acceleration occurs, has an order of one tenth of a percent.

All these data refer to anhydrous NG. In separate works there are indications on the accelerating influence of water on decomposition of nitroglycerine or powders on its base [4], [10]. These indications, however, have either an indirect, or qualitative character. At the same time the influence of water on decomposition of NG presents significant and many-sided interest. Commercial nitro esters and different mixtures, in the composition of which it enters, always contain a certain quantity of water. NG esters are able to be hydrolyzed. Hydrolysis will form products of an acid character, which can accelerate it. Side by side with this, the products of hydrolysis, entering the oxidizing-reduction reactions, will form, in particular, water, which also can promote acceleration of decomposition. In connection with this, it was expedient to study the influence of water on decomposed NG.

The results of this investigation, conducted basically by a method of measurement of pressure of formed gases with the help of a manometer of the Bourdon type [1], constitute the contents of this article.

Experimental Part

Obtainment and Purification of Nitroglycerine

NG was obtained by nitrating of dynamite glycerine with an anhydrous mixture of chemically pure sulphuric and acetic acids (1 : 1) at a temperature of 15°. After multiple washing by a 3% solution of soda and water, NG contained neither acid, nor alkali, and had a temperature of hardening of 12.2°

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[1] Description of the method, its advantages and weak sides is given in [2].

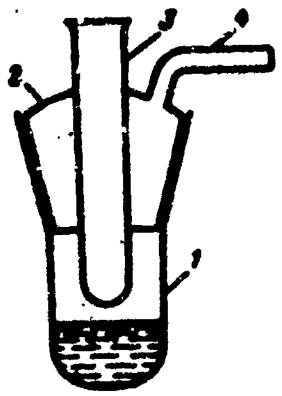

Fig. 1. Instrument for molecular distillation of nitroglycerine. 1-cone, 2-cover, 3-branch, 4-drain.

In order to avoid the possible influence of impurities in NG, it was subjected to purification. Multiple crystallization from a fusion, both in stable, and also in labile form turned out not to be very effective: after three-phase recrystallization, the temperature of hardening was raised only by 0.2°. Therefore recrystallization from the esters was undertaken. After octuple recrystallization, the NG, liberated from esters by prolonged evacuation, had a temperature of hardening of 13.0°. Further recrystallization did not increase this magnitude.

It is possible to purify NG also by molecular distillation. The advantage of this method includes, in particular, the fact that in NG any solvent is not introduced, to be completely liberated from which is quite difficult. This distillation was conducted in the instrument depicted in Fig. 1.

Into a cone 1 was poured a small quantity (30-40 g) of NG. The cone was covered with a polished cover 2 having a digitate branch 3, where it was flooded with liquid nitrogen. A drain 4 was joined to the high-vacuum installation. Distillation was conducted at residual pressure of 10^{-4} - 10^{-5} mm Hg. The NG was heated to 40-50°. Upon settling in the digitate branch, the product was collected, and for investigation an average fraction was applied. After the first distillation the NG became completely colorless and had a temperature of hardening of 12.9°, and after the second (and third) operation 13.1°. The nitroglycerine, recrystallized 8 times from the esters and then subjected to molecular distillation, had the same temperature of hardening.

V. V. Gorbunov undertook an attempt to purify NG by means of recrystallization of it from concentrated nitric acid (90%), not containing oxides of nitrogen. After double recrystallization and washing from acid a product was received with a temperature of hardening of 13.0°.

From all of these methods, molecular distillation is the safest, most reliable and comparatively simple method of purification of nitroglycerine.

Preparation of the Experiment

NG was thoroughly freed from volatile impurities, which can affect its disintegration. For that, a system of collected instruments (fig. 2) with nitroglycerine in a reaction vessel 1 was pumped at first by a rotary, and then a diffusion pump to a residual pressure of 10^{-4} -10^{-5} mm Hg. It is difficult to completely remove all volatile substances dissolved in NG. Alternate cooling by liquid nitrogen and heating of the reaction vessel with warm (30-40°) water with continuous evacuation facilitates their removal. Probably, as a result of convection mixing of the liquid occurs, which accelerates separation from it of dissolved volatile substances. For mixing of the liquid it is possible to also use a magnetic mixer. In order to ensure completeness of removal of volatile substances, nitroglycerine especially in large weights usually for the duration of 24-hours was under a vacuum. In this case an increase of pressure was not observed in the reaction vessel after submersion of it into a thermostat and brief heating (2-3 minutes); otherwise the pressure increased by several millimeters of the mercury column.

For introduction of water after evacuation of the system and freeing NG from volatile soluble impurities cocks a and f were closed before the reaction vessel. From the tube preliminarily filled by water [1] before cock d, a little of its quantity was introduced in the space between cocks c and d, whence the water vapors upon opening cock c filled the entire system, including the sphere 2.

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[1] Water before introduction of it into the tube was boiled for removal of air dissolved in it.

The pressure of water vapors (measurement of it was done by a manometer 4), in order to avoid possible condensation, always was less than the steam pressure at room temperature and was 10-12 mm Hg at 20° (pressure of aqueous saturated vapor is equal to 17.5 mm Hg at the same temperature). Then cock b was closed and the water vapors in the sphere 2, were transferred into the reaction vessel 1. For that cock a was opened upon cooling the reaction vessel by liquid nitrogen. Water practically was instantly condensed in the vessel which one could see by the return of the needle of the manometer 1 to zero position.

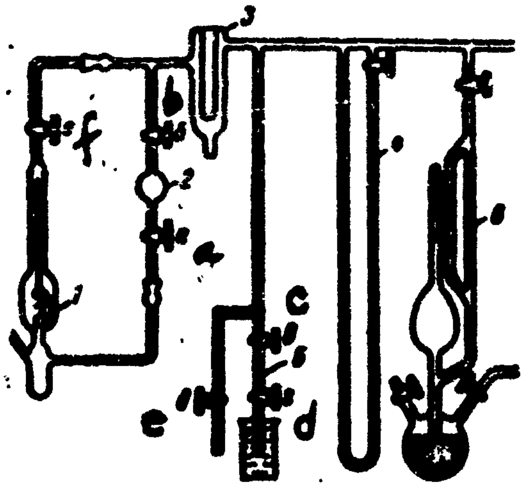


Fig. 2. Diagram of installation for preparation of experiments.

1)reaction vessel with diaphragm manometer, 2)sphere for dosage of water and determination of volume of reaction vessel, 3)trap, 4)mercury manometer, 5)attachment for dosage of water, 6)McLeod manometer. a, b, c, d, e, f -cocks.

Knowing the volume of the sphere, pressure and temperature of the water vapors in it, one can determine the quantity of water introduced into the reaction vessel. By measuring the pressure of H_2O vapors and the number of operations, it is possible to introduce into the reaction vessel any necessary quantity of water. However, V. V. Gorbunov [3] established that with such methodology, more water was introduced into the reaction vessel than was assumed. This, apparently, is explained by the adsorption of its vapors on the wall of the sphere and condensation in the form of a fine film. Therefore in the sphere the water was more calculated according to the law of ideal gases. In order to avoid this, V. V. Gorbunov warmed up the ball with water vapors to 60 /-100°/; with this temperature the pressure of saturated vapor constitutes 149-760 mm Hg which decreases the adsorption of water vapors on the walls of the vessel and, besides, allows to work in a range of pressures (20-50 mm Hg), far from the pressures of saturated vapor at a given temperature, without lowering and even with an increase of accuracy of measurement p_{H_2O}. By this methodology, introducing a definite quantity of water into the vessel with NG and measuring the equilibrium pressure of its vapors above nitro esters, the investigator determined the solubility of water in NG at 40, 60, 80, and 100°. These values of solubility were used in this account for determining the total amount of water in the reaction vessel.

When large quantities of water were required, it was introduced into the reaction vessel by a pipette. To avoid volatilization of the water, evacuation of system was accomplished with continuous cooling of the reaction vessel by liquid nitrogen.

After introduction of water into the reaction vessel, the bank on the tube, connecting it with the vacuum system, was resealed, and the diaphragm device was ready for the experiment. For carrying out the experiment the device was lowered into a thermostat in such a manner so that the whole reactionary volume was at the temperature of the experiment. The time of heating of the reaction vessel constituted 2-3 minutes. Usually the experiment was finished after the achievement of atmospheric pressure, but in certain cases it was led to a final pressure, equal to ~ 2000 mm Hg.

After termination of the experiment, the diaphragm device was removed from the thermostat, and pressure p_{room} was measured of the products which did not condense at room temperature. Knowing p_{room} and pressure at the temperature of the experiment, it is possible to calculate a conditional quantity of gases, condensed at room temperature, by the equations:

$$B = 100 - A;$$

$$A = \frac{\text{[illegible]}}{p_{room}} \cdot 100,$$

where A — % of noncondensing gases;

B — % of gases condensed at room temperature;

p — pressure in reaction vessel at temperature of the experiment T (°K), mm Hg;

p_{room} — pressure in reaction vessel at room temperature T_{room} (°K), mm Hg.

This calculation is conditional, since in the calculation of B, the vapor pressure of condensed gases and their solubility in NG will be disregarded, and it is assumed that the reaction is stopped immediately after extraction of the reaction vessel from the thermostat.

The thermostat was a glass vessel with a capacity of 10 liters, insulated on the outside with asbestos and filled with a liquid (dibutylphthalate, glycerine or mineral oil), the heating of which was accomplished by a Nichrome spiral dipped in it. Homogeneity of temperature in the thermostat was attained by mixing the liquid of propeller mixer, set into motion by an electric motor. Constancy of temperature was maintained by means of a contact thermometer with a magnetic head of the TKM type, united with a relay, turning off or turning on the heater with the increase or lowering of temperature above or below what was given. Temperature was measured by a range thermometer. Its fluctuations did not exceed ± 0.1 at 100°.

Results of Experiments

Water is poorly soluble in nitroglycerine, and therefore, its content in it can be changed only in relatively narrow limits. This is attained by the change of pressure of water vapors above nitro esters. According to the law of Henry, the concentration of water in NG should be proportional to this pressure. However in the course of decomposition, apparently, under the influence of its products, solubility of water in nitroglycerine can strongly increase.

Dissolved water can be combined also chemically. Therefore, not only water plays a role, initially dissolved in NG, but also its complete quantity in the reaction vessel.

An essential influence on the course of the process is rendered by the relationship between volumes of NG and the reaction vessel, i.e., the degree of filling of the latter $\left(\delta = \frac{v_{NG}}{v_r}\right)$, since it determines pressure at a given degree of disintegration of a substance, and consequently, the concentration of gas products of decomposition in the liquid. In addition, on magnitude δ depends the distribution of water between the liquid and gas phases. The solubility both of water, and also the products of disintegration in NG, and also the speed of reaction is influenced by the temperature. Thus, the flow of disintegration of nitroglycerine in the presence of water depends on a number of partially mutually connected factors.

The quantity of water introduced into the reaction vessel was judged by the equilibrium pressure of its vapors (p_{H_2O}). Knowing the solubility of H_2O in NG, it is possible by this pressure to calculate the quantity of water dissolved in nitro esters and in the gas phase, and consequently, the total quantity of water in the reaction vessel.

The quantity of water in liquid phase is calculated by the formula:

$$g_l = kp_{H_2O}m; \ \% \text{ by weight } H_2O_l = kp_{H_2O} \cdot 100,$$

where g_l -- quantity of water in NG in g;

p_{H_2O} -- equilibrium pressure of water vapors in reaction vessel in mm Hg;

k -- quantity of water in g, dissolved in 1 g of NG with pressure of its vapors in 1 mm Hg;

m -- weighed amount of NG in g.

Percentage of water in NG at a given temperature is determined only by the pressure of water vapors.

The amount of water in the gas phase is approximate, but with sufficient accuracy is determined according to the law of ideal gases:

$$g_g = \frac{p_{H_2O} v M}{RT}; \ \% \text{ by weight } H_2O \text{ g. p.} = \frac{p_{H_2O} v M 100}{mRT},$$

Table 1

Influence of small quantities of water on decomposition nitroglycerine

t °C	m г a)	δ·10⁴	p_{H_2O} мм рт. ст. b)	% вес. H_2O c)	$\left(\frac{\Delta V}{\Delta \tau}\right)_{нач}$ см³/г·мин d)	τ_{700} мин. e)
100°	0,2044	329	0	0	0,00129	2370
	0,2410	304	8	0,0204	0,00193	1665
	0,2172	271	14	0,0383	0,00166	1420
120°	0,0643	57	0	0	0,034	1390
	0,0556	63	10	0,079	0,042	1260

Conditional designation:
m—weighed amount of NG; δ —degree of filling; p_{H_2O}—equilibrium pressure of water vapors in the reaction vessel; % by weight H_2O—total quantity of water in reaction vessel, with respect to NG; $\left(\frac{\Delta V}{\Delta \tau}\right)_{initial}$ -- initial speed of gas formation, τ_{700} —time of achievement of pressure 700 mm Hg, which corresponds to the stage of sharp acceleration of gas formation.

a) grams; b) mm Hg; c) % by weight; d) $\left(\frac{\Delta V}{\Delta \tau}\right)_{initial}$, n cm³/g .min. ; e) minutes.

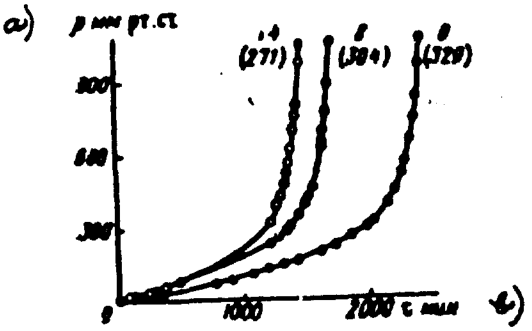


Fig. 3. Decomposition of NG in the presence of small amounts of water at 100° and δ ≈ 0.03.

Numbers by curves —equilibrium pressure of water vapors and δ·10⁴ (in parentheses).

a) p mm Hg; b) τ minutes.

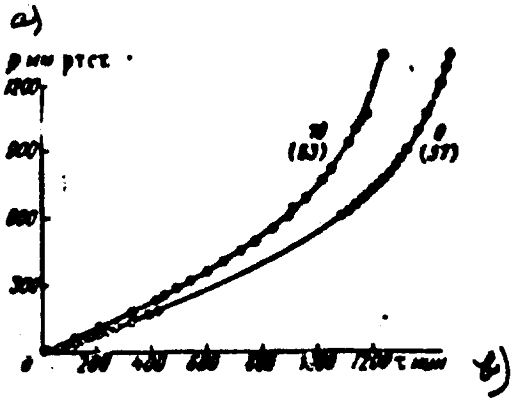


Fig. 4. Decomposition of NG in the presence of small amounts of water at 120° and δ ≈ 0.006.

Numbers by curves —equilibrium pressure of water vapors and δ·10⁴ (in parentheses).

a) p mm Hg; b) τ minutes.

40 to 29 and 24 hours, correspondingly.

As in the case of anhydrous NG, in the presence of small quantities of water, the gas phase, colorless in the beginning, becomes brown in the course of decomposition (NO_2), and the intensity of color is gradually strengthened.

Analogously proceeds disintegration and at lower temperatures. Thus, according to the data of M. S. Plyasunov at 60° and $\delta = 0{,}80$ ($p_{H_2O} = 29$ mm Hg) 360 hours after the beginning of the experiment, sharp acceleration of gas formation sets in; dry NG provided it in 550 hours ($\delta = 0{,}85$).

Decomposition of Nitroglycerine in the Presence of Moderate Quantities of Water

The origninal dependence of the change of pressure in time was observed in moderate quantities of water in the reaction vessel. Moderate quantities of water is a relative concept; their lower limit little depends on δ and temperature and corresponds to the equilibrium pressure of H_2O vapors approximately 30-50 mm Hg. The upper limit as will be shown below greatly depends on these factors.

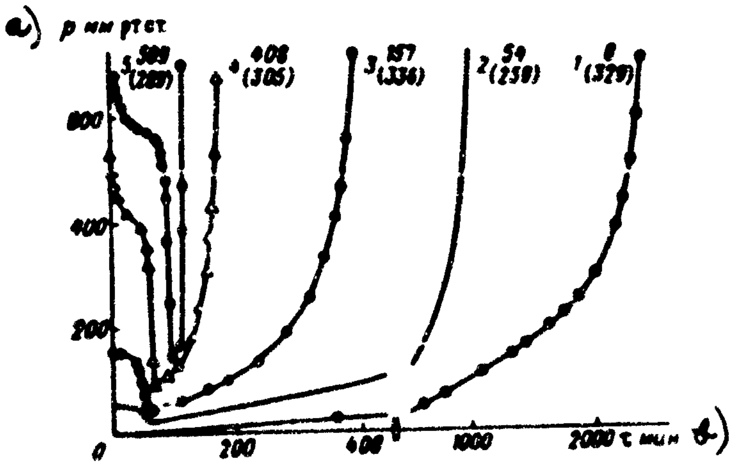


Fig. 5. Decomposition of NG in the presence of moderate quantities of water at 100° and $\delta \approx 0.03$.

Numbers by curves-the ordinal number of the curve, equilibrium pressure of water vapors and $\delta \cdot 10^4$ (in parentheses).

a) p mm Hg; b) τ minutes.

At 100°, $\delta \approx 0,03$ and different pressures of water vapors (50 mm Hg and higher) the process proceeds in the following form. If there is comparatively little water, then after submersion of the reaction vessel in the thermostat, the pressure in it will quickly be raised due to the evaporation of water, and then for a certain time remains constant (fig. 5, curves 2 and 3). If however, there is much water, then it is evaporated faster, than it is dissolved in NG. Therefore, in the beginning the pressure is above equilibrium (curves 4 and 5), and then it more or less quickly (after 30-50 minutes) decreases to its own equilibrium value. An increase of the surface of NG and, consequently, a decrease of the thickness of its layer reduces this time. Thus, with an increase of surface by 3 times, the time of attainment of equilibrium pressure was reduced to 10 minutes, i.e., was significantly less than in the first case.

After attainment of equilibrium pressure, it remains constant for a certain time, then quickly falls to a certain minimum value (p_{min}), , after which a more or less accelerated growth begins. At the end of the fall of pressure, the gas phase acquires a weak brown color, gradually becoming stronger in the course of further decomposition (NO_2).

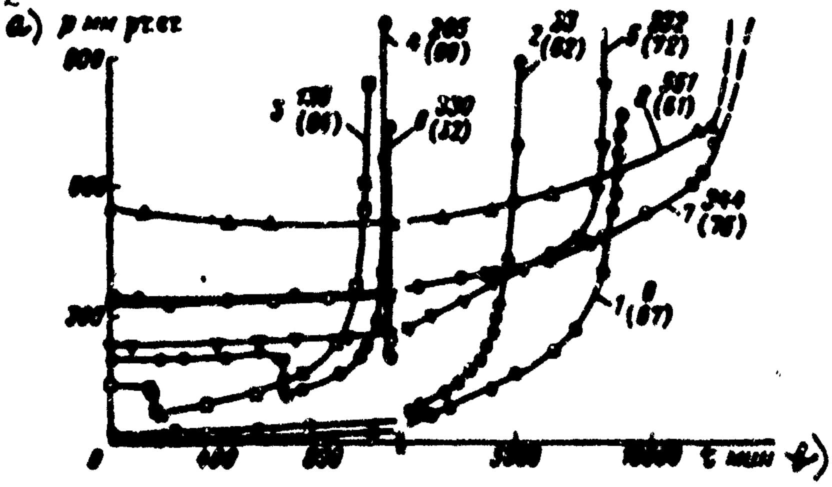


Fig. 6. Decomposition of NG in the presence of water at 100° $\delta = 0,0080$ and $0,0075$.

Numbers by curves the ordinal number of the curve, equilibrium pressure of water vapors and $\delta \cdot 10^4$ (in parentheses).

a) p mm Hg; b) τ minutes,

The same character of disintegration of NG in the presence of water was observed at $\delta \approx 0.006$ and temperatures of 100 and 120° and at $\delta \approx 0.03$ and 80° (fig. 6, 7, 8).

As can be seen from the graphs, the time up to the approach of the fall of pressure - the induction period - strongly fluctuates, and in general is observed the tendency for it to grow with an increase of the quantity of water. At 100° and $\delta \approx 0.03$ with an increase of p_{H_2O} from 54 to 570 mm Hg (fig. 5) the induction period is increased from 35 to 70 minutes. It is necessary to note that in this case due to the relative slowness of dissolution and the small-in-magnitude induction period, the moment of achievement of equilibrium pressure and the beginning of its fall is less clear, than at small δ and lower temperatures, with which the induction period is greater.

Stronger fluctuations of the induction period were observed at low temperatures and small δ. Thus at 30° and $\delta \approx 0.03$ (fig. 8) the period of constancy of pressure with a change of pressure of water vapors from ~ 60 to ~ 240 mm Hg fluctuates from 600 to 2200 minutes. At one and the same temperature, a stronger change of time to the beginning of lowering of pressure with an increase of p_{H_2O} was noted at small δ. An increase of p_{H_2O} from 136 mm Hg at $\delta \approx 0.0065$ (fig. 6, curve 3) to 330 mm (fig. 6, curve 6) leads to an increase of the induction period from 180 to 1100 minutes, whereas at $\delta \approx 0.003$ approximately in that same range of pressures, this magnitude, from 35 minutes (fig. 5, curve 2) increases only to 50 minutes (fig. 5 curve 4) and even at p_{H_2O} = 560 mm Hg (fig. 5 curve 5) it constitutes only 70 minutes.

An increase of temperature decreases not only the magnitude of the induction period, but also the range of its fluctuations depending upon the content of water. Thus, at 120°, p_{H_2O} = 229 mm Hg and $\delta \approx 0.0063$ (fig. 7, curve 3) its magnitude constitutes 15 minutes and changes comparatively little with an increase of equilibrium pressure of water vapors: even at p_{H_2O} = 1409 mm Hg (fig. 7, curve 7) the time to the beginning of lowering of pressure is increased only by 2 times.

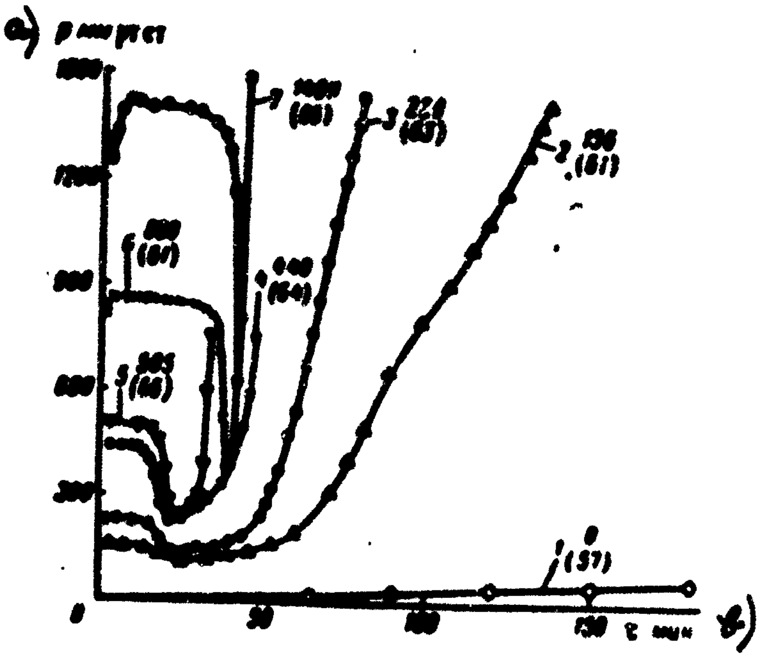
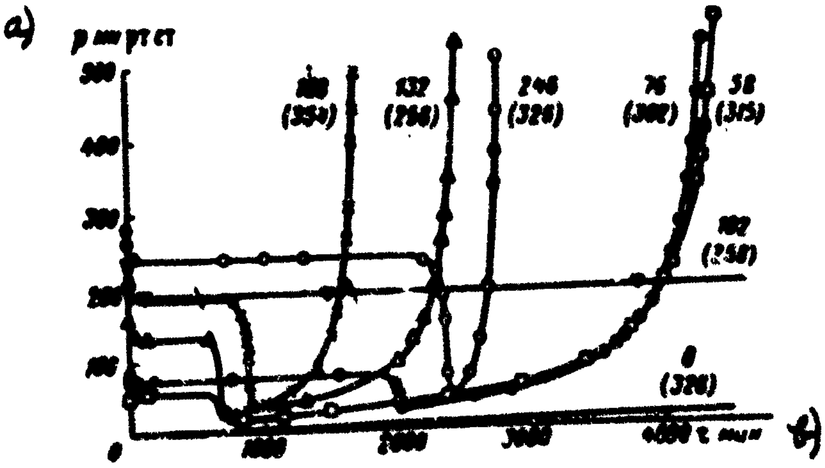


Fig. 7. Decomposition of NG in the presence of water at 120°
δ=0,0061 , /, -0,0098 .

Numbers by curves-the ordinal number of the curve, equilibrium pressure of water vapors and $\delta \cdot 10^4$ (in parentheses).

a) p mm Hg; b) τ minutes.



[illegible] Decomposition of NG in the presence of water at 80°
[illegible] -0,0252 , / 0,0061

Num[illegible] curves the equilibrium pressure of water vapors and $\delta \cdot 10^4$ (in parentheses).

a) p mm Hg; b) τ minutes.

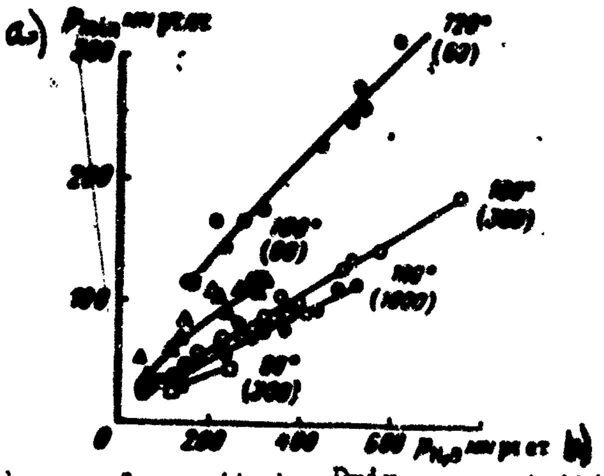


Fig. 9. Dependence of magnitude Pmin on initial pressure of water vapors in the decomposition of NG in their presence.

Numbers by curves—temperature of experiment and $\delta \cdot 10^4$ (in parentheses).
a) p_{min} mm Hg; b) p_{H_2O} mm Hg.

Fall of pressure occurs with an increasing speed, which then decreases. Time of fall of pressure constitutes: at 120° and $\delta \approx 0.006$ approximately 7-10 minutes, at 100° and $\delta \approx 0.006$, 20-50 minutes, at 100° and $\delta \approx 0.03$, 35-45 minutes, at 80° and $\delta \approx 0.03$, 160-240 minutes.

With an increase of initial pressure of water vapor at one and the same δ, p_{min} is increased (fig. 9). In fig. 10 are curves $\frac{p_{H_2O}-p_{min}}{p_{H_2O}} = f(p_{H_2O})$. From the graphs in fig. 9 and 10, it is clear that an increase of temperature leads to an increase of p_{min}, and consequently, to a decrease of the relative magnitude of fall of pressure.

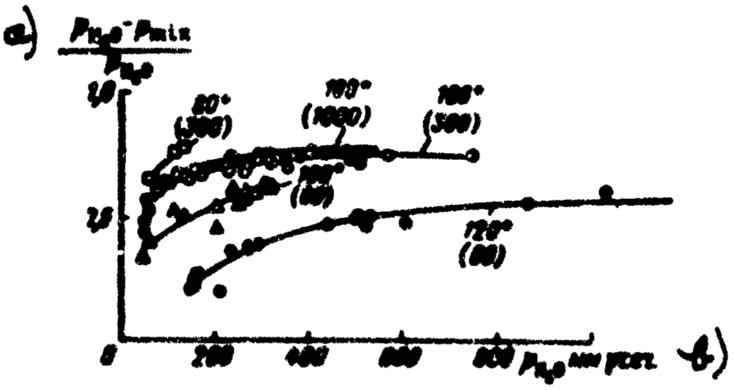


Fig. 10. Dependence of relative magnitude of fall of pressure on initial pressure of water vapors in the decomposition of NG in their presence.

Numbers by curves—temperature of experiment and $\delta \cdot 10^4$ (in parentheses).
a) $\frac{p_{H_2O}-p_{min}}{p_{H_2O}}$; b) p_{H_2O} mm. Hg.

After achievement of the minimum, a more or less accelerated growth of pressure begins. As can be seen from the graphs in fig. 5-8, an increase of initial pressure of water vapors leads to an increase of the speed of growth of pressure and reduction of time from the moment of passage of p_{min} to the beginning of sharp acceleration of gas formation.

The magnitude of the weighed amount of NG very weakly affects the duration of the induction period. From fig. 11 it is clear that an increase of the weighed amount of NG by approximately 24 times at one and the same δ , in the presence of ~ 1% by weight water, practically does not change the magnitude of the induction period, but by one third by (by ~ 40 minutes) reduces the time to the beginning of sharp acceleration of gas formation after passage by pressure of its minimum.

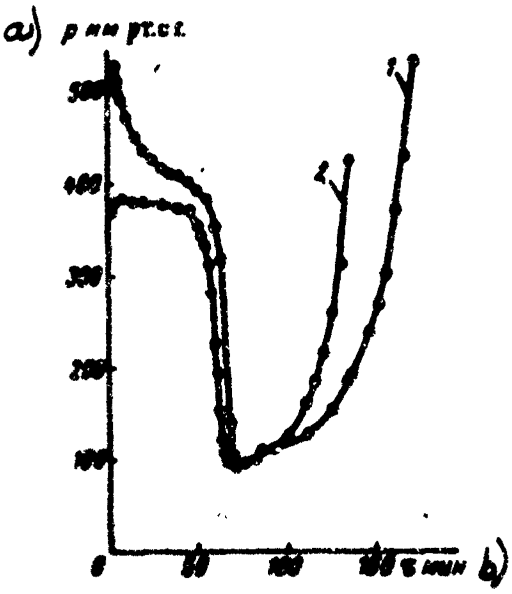


Fig. 11. Influence of magnitude of weighed amount of NG on its decomposition in the presence of water.

1- p_{H_2O} = 408 mm Hg (1.04% by weight), δ = 0.0305, m = 0.1841 g; 2- p_{H_2O} = 382 mm Hg (1.04% by weight), δ = 0.0275, m = 4.4085 g.

a) p mm Hg; b) τ minutes.

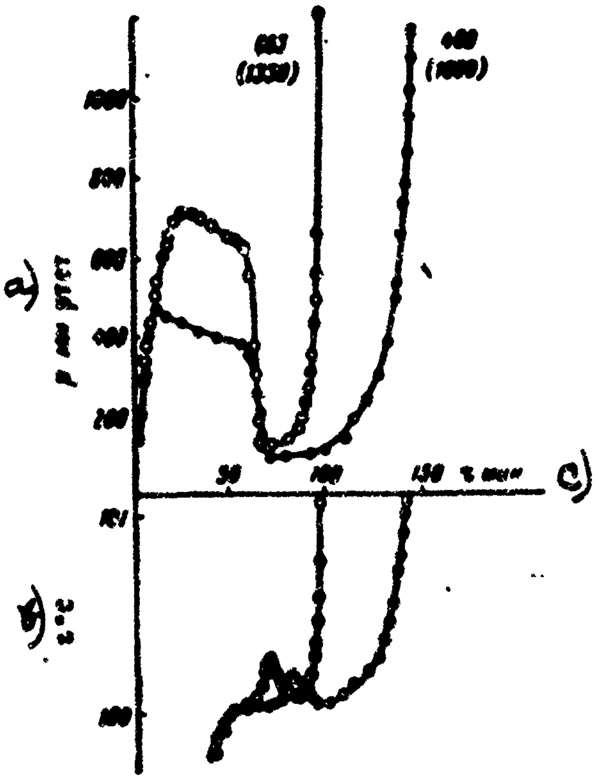


Fig. 12. Change of temperature of NG during its decomposition in the presence of water at 100°.

Numbers by curves—pressure of water vapors and δ ·10^4 (in parentheses).

a) p mm Hg; b) t °C; c) τ minutes.

A known role can be played by the magnitude of the surface of the liquid and the thickness of its layer, since these factors determine the ease of diffusion, on the one hand, of water vapors in NG and, on the other hand, of gases, forming during its decomposition.

A somewhat faster acceleration of the reaction after p_{min} with a large weighed amount of NG can be connected self-heating due to the heat, emanating during the reaction. The experiments, conducted jointly with B. S. Svetlov, on the determination of the temperature of NG decomposed under conditions approaching adiabatic, showed that a fall of pressure is accompanied by a small, but clearly noticeable increase of temperature of NG (fig. 12), and even greater, the higher the content of water.

Thus, in the presence of 0.59 and 0.86% by weight water, the temperature of NG exceeds the thermostat temperature (100± 0.05°) by 0.19 and 0.27° correspondingly. Then the temperature falls to the thermostat temperature. At the stage of accelerated growth of pressure, the temperature of NG is increased significantly greater and becomes higher than the thermostat temperature by more than 3° upon achievement in the reaction vessel of a pressure of 1420 mm Hg.

In order to determine how the quantity of gases changes, which are condensed at low temperature, in the course of decomposition of NG in the presence of water, the reaction vessel from time to time was removed from the thermostat, and pressure was measured in it at 20 and 0 °. By the pressure at the temperature of the experiment 80° (this temperature was selected, so that the induction period is sufficiently great) and at 20 and 0° the content of condensing gases was determined. Results of the experiment are in fig. 13. In the induction period, the pressure both at high temperature (80°), and also at low (20 and 0°) changes little; consequently, the quantity of condensed gases remains approximately constant. Fall of pressure is accompanied by a decrease of the content of condensed gases; with the subsequent growth of pressure, their quantity is increased. It is necessary to note that gases

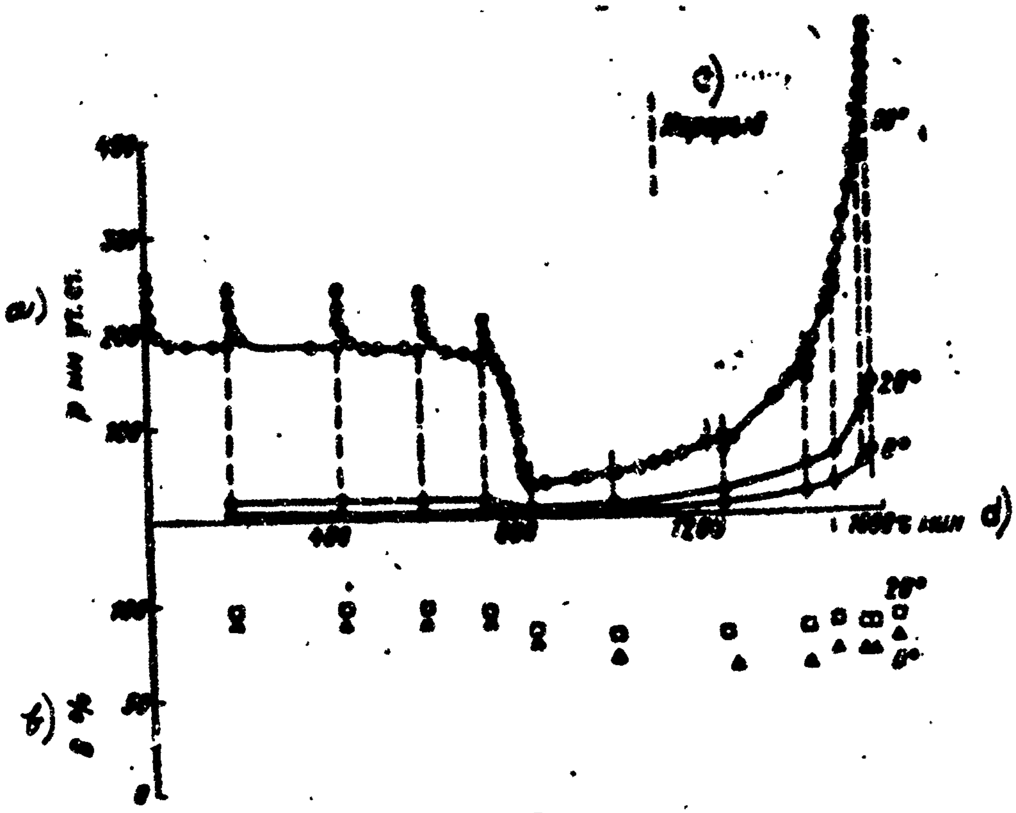


Fig. 13. Change of pressure and amount of condensed gases (B) at 20 and 0° in the process of decomposition of NG at 80° in the presence of water.

a) p mm Hg; b) In %; c) Intèruption; d) τ minutes.

not condensed at the temperature of liquid nitrogen, appear only at the stage of sharp acceleration of gas formation.

Influence of Large Amounts of Water on Decomposition of NG

The characteristic picture of decomposition of NG in the presence of a moderate quantity of water, described in the preceding division, with a further increase of the content of H_2O changes again. Thus, in the experiment with p_{H2O} = 551 mm Hg ϕ = 0.0061, in the beginning we observed not a sharp, but slow and small-in-magnitude fall of pressure: (fig. 6, curve 8 and fig. 14, curve 7) pressure after 1320 minutes fell to 36 mm Hg. After achievement of the minimum it began, but again slowly, to grow with a speed, approximately equal to the initial speed of gas formation in decomposition of anhydrous NG. Sharp acceleration of gas formation occurred/ significantly later, than it was observed in the decomposition of not only moist, but also anhydrous NG. Thus, in that same experiment (fig. 14, curve 7) after 180 hours (~ 11,000 minutes) the pressure in 3 hours grew to ~2 at. Anhydrous NG in these conditions begins spreading rapidly already after 135 hours, but the presence of water reduces this time even to 17 hours.

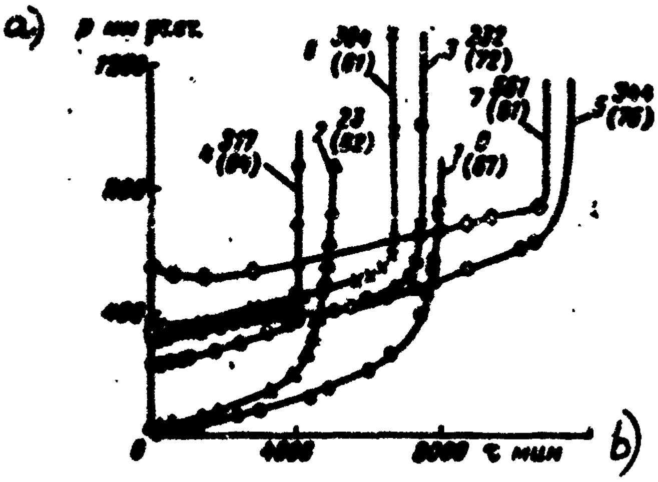


Fig. 14. Decomposition of NG in the presence of water at 100° and $\delta \approx 0.006$.

Numbers by curves—ordinal number of curve, equilibrium pressure of water vapors and $\delta \cdot 10^4$ (in parentheses). a) p mm Hg; b) τ minutes.

During the period of the entire experiment up to the beginning of sharp acceleration of growth of pressure, the gas phase remained colorless; after which there appeared a brown color, increasing in intensity with time. The same phenomenon was observed also at a somewhat smaller equilibrium pressure of water vapors (364 mm Hg, see fig. 14, curve 6). The distinction includes only the time to the beginning of sharp acceleration of gas formation.

If the speed of gas formation in a given case characterizes the speed of the reaction, then we must conclude that with a large content of water, its influence, in the sense of acceleration, decreases.

It is necessary to add that in separate experiments both at 100° $\delta \approx 0.006$, and also at 30° $\delta \approx 0.03$ the usual picture of the influence of water was not observed (constancy of pressure, fast fall and subsequent more or less fast growth of it) and in that area of pressure of vapors of the latter, for which it is characteristic. Thus, for example, at 100° and $p_{H_2O} = 344$ mm Hg (fig. 14, curve 5) for a long time pressure slowly grew and only after ~180 hours, the growth of it began to be quickly accelerated; in addition the time to the beginning of sharp acceleration of gas formation was significantly greater, than it was observed in the decomposition of not only moist, but also even anhydrous NG.

Such a picture was observed also at 80° (p_{H_2O} = 192 mm Hg; $\delta \approx 0.0258$) (fig. 8); there was no acceleration of gas formation for the duration of 690 hours, and during that time pressure grew to 100 mm Hg. This indicates that some factors outside of the control of the experimenter could appear to have an essential influence on the process of transformation in the presence of water and, in particular, in periods of the approach of sharp acceleration of disintegration. Apparently, the role of these factors increases with the lowering of temperature and decrease of δ, since such an effect was not observed at higher temperature (120°, $\delta \approx 0.006$), and also with a larger degree of filling (100° and $\delta \approx 0.03$). With these last conditions, the described change of character of curve $p = f(\tau)$ was not observed even at an increase of initial pressure of water vapors almost to 760 mm Hg. Addition of a still larger quantity of water (11%), with which it is under the conditions of the experiment not only in solution, but also in a liquid-drop state turbid NG, significant extends the induction period (to ~6 hours); then a very small fall of pressure occurs, passing in its growth with a very high speed (fig. 15).

One should note that before the beginning of fall of pressure, the water, apparantly, under the influence of the formed acid is completely dissolved in the NG which may be marked by the disappearance of turbidity.

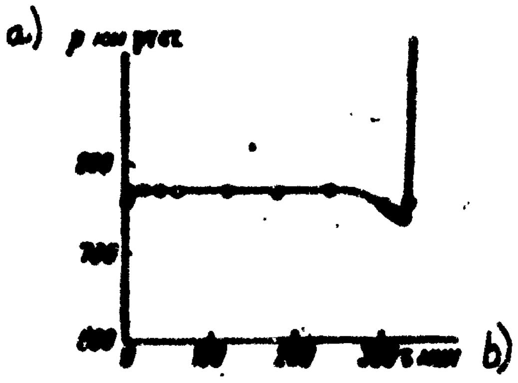


Fig. 15. Decomposition of NG in the presence of 11.04% by weight, water at 100° and $\delta = 0.034$.

a) p mm Hg; b) τ minutes.

Influence the Size of the Surface of Contact of Nitroglycerine With Glass on the Disintegration of This Explosive in the Presence of Water [1]

Strong variations of magnitude of the induction period and its significant increase, observed in certain experiments on the decomposition of NG in the presence of water, can be connected with the influence of the surface of the reaction vessel, the state of which is difficult to control. In order to explain the possibility of such an influence, experiments were performed with an increased surface of contact of NG with steklom. This was attained by filling the reaction vessel with glass capillaries or spun glass. The capillaries (external diameter 0.4-0.5 mm, length 3-4 mm) were completely coated with NG, whereupon the surface of contact of nitro esters with glass was increased by 3-10 times. A greater increase of surface was attained by the application of spun glass, on which the nitroglycerine was spread. The experiments were conducted at 100° and $\delta \approx 0.03$, i.e., such conditions, in which an anomalous significant increase of time to the beginning of sharp acceleration of gas formation was not observed, and variations of magnitude of the induction period were insignificant.

As can be seen in the graph (fig. 16), the increase of surface by 3-10 times did not change the general form of curve $p = f(\tau)$, but somewhat increased the time to the beginning of the fall of pressure. Thus, in the experiment, where equilibrium pressure of water vapors constituted 398 mm Hg (curve 1), the time of achievement of minimum pressure was increased by 20 minutes as compared with the usual experience (p_{H_2O} = 408 mm Hg, curve 2). The same increase of this time was observed also at smaller p_{H_2O} (cf. curves 3 and 4). The increase of the surface did not render a significant influence on the **subsequent** development of the process of disintegration.

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[1] These experiments were conducted by student A. G. Kazakevich.

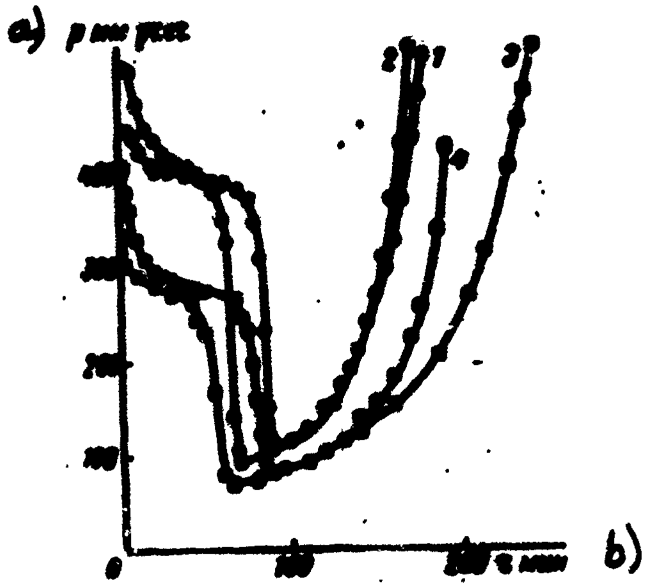

Fig. 16. Influence of filling of a reaction vessel with capillaries on the decomposition of NG in the presence of water at 100°.

1- with filling, [illegible] p_{H_2O}–[illegible] mm Hg;
2- without filling, [illegible] p_{H_2O}–[illegible] mm Hg;
3- with filling, [illegible] p_{H_2O}–[illegible] mm Hg;
4- without filling, [illegible] p_{H_2O}–[illegible] mm Hg

a) p mm Hg; b) τ minutes.

A strong increase of the induction period was observed upon filling the reaction vessel with spun glass, increasing the surface approximately by 30 times. In this case at p_{H2O} = 325 mm Hg the duration of the induction period from 76 minutes grew to 160 minutes (fig. 17, curve 2).

It is interesting to note that the same retarding action is rendered by spun glass, which is in direct contact with the NG [1]. In this case at a pressure of water vapor, equal to 330 mm Hg (curve 3) the magnitude of the induction period was approximately the same, as in the case of disintegration of NG distributed on spun glass (τ min was 156 and 159 minutes, correspondingly).

A still stronger influence of the surface was exhibited with a large initial pressure of water vapor. Thus, in the experiment where p_{H_2O} = 460 mm Hg (curve 4), the duration of the induction period constituted 900 minutes, i.e., almost by 15

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[1] The spun glass was inside the diaphragm manometer, the NG—on the bottom of the reaction vessel.

times exceeded the usual duration.

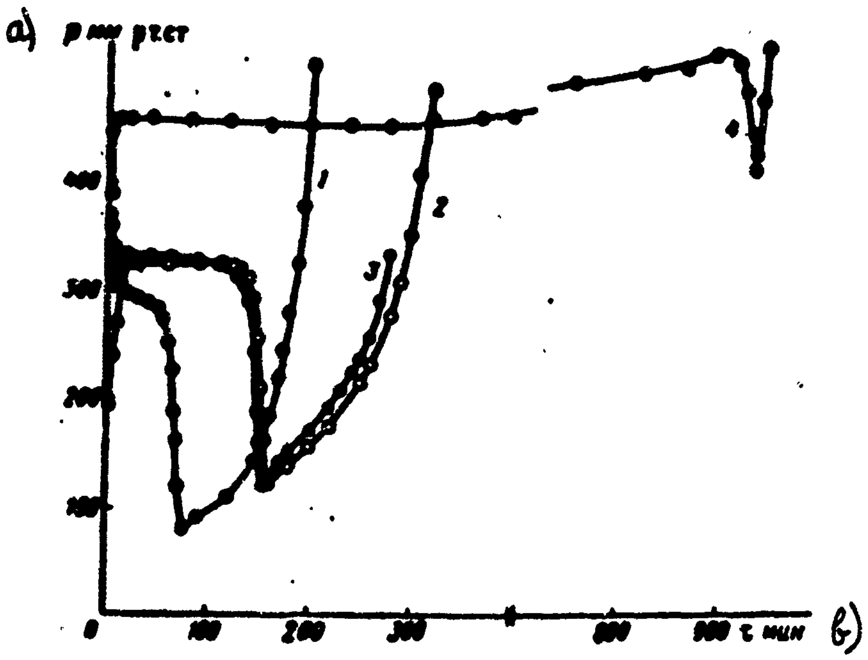

Fig. 17. Influence of filling of reaction vessel with spun glass on the decomposition of NG in the presence of water at 100°.

1- without filling, $\delta = 0.0367$, $p_{H_2O} = 293$ mm Hg; 2- with filling, $\delta = 0.0350$, $p_{H_2O} = 325$ mm Hg; 3- with filling above NG, $\delta = 0.03$, $p_{H_2O} = 330$ mm Hg; 4- with filling, $\delta = 0.0291$, $p_{H_2O} = 460$ mm Hg.

a) p mm Hg; b) τ minutes.

Such a character of decomposition of moist NG in reaction vessels with filling shows that the magnitude of the surface of glass, possibly due to its weakly-alkaline character, can render an essential influence on the disintegration NG, significantly increasing the time to the beginning of sharp acceleration of gas formation, especially with large quantities of water. Probably, this is partly possible to explain by those variations in the magnitude of the induction period, which were observed in the disintegration of NG in the presence of water.

Influence of Degree of Filling of Vessel (δ) on Decomposition of Nitroglycerine in the Presence of Water

An increase of the degree of filling of the reaction vessel signifies an increase of pressure of the products of decomposition of NG at one and the same degree of its disintegration and, consequently, an increase of the contents of soluble gas products in NG. This leads to earlier achievement of critical pressure of gas products, after which, pressure starts to grow sharply.

In that case, when water is present, an increase of the degree of filling at a given initial pressure of its vapors, in addition, signifies a decrease of the total quantity of water with respect to NG at constant initial content of it in liquid phase.

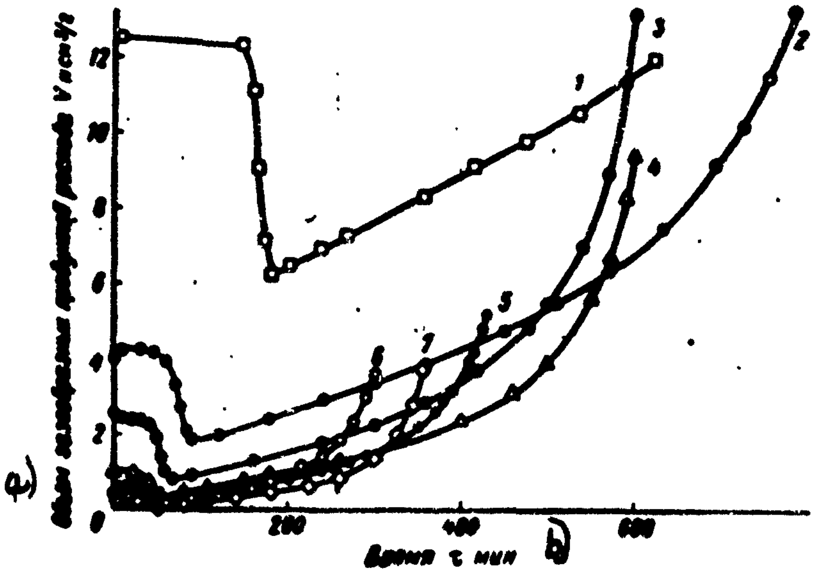

Fig. 13. Influence of degree of filling of reaction vessel on decomposition of NG at 100°.

1- δ = 0.0065, p_{H_2O} = 136 mm Hg; 2- δ = 0.0126, p_{H_2O} = 90 mm Hg; 3- δ = 0.0234, p_{H_2O} = 117 mm Hg; 4- δ = 0.0547, p_{H_2O} = 96 mm Hg; 5- δ = 0.0927, p_{H_2O} = 101 mm Hg; 6- δ 0.113; p_{H_2O} = 117 mm Hg; 7- δ = 0.248, p_{H_2O} = 104 mm Hg.

a) Volume of gas production of disintegration, Vn cm^3/g;
b) Time τ minutes.

The influence of the degree of filling of a reaction vessel was studied at 100° and initial pressure of water vapor ~ 100 mm Hg, whereupon δ changed in a range from 0.0065 to 0.25 (fig. 13). For the possibility of comparison of results of the experiments at different δ on the graph along the axis of ordinates is the volume (taking into account water) of gases, emanating during decomposition, referred to 1 g NG, brought to normal conditions. Initial and certain other data of these experiments are in table 2.

For all these δ, the form of curve $P = f(\tau)$ is the same (see fig. 13): period of constancy of pressure, its fall and subsequently more or less fast growth. Increase of δ leads to a decrease of the relative quantity of water and correspondingly to a reduction of the magnitude of the induction period. According to the data of B. B. Gorbunov at the most possible δ, the induction period consitiutes ~ 30 minutes (τ min at δ = 0.857 - 43 minutes). After passage by pressure of the minimum, the accelerated development of the process proceeds faster, the greater the δ.

Table 2

Influence of degree of filling of reaction vessel on decomposition of NG in the presence of water at 100°.

a) $m_{НГ}$, г	$\delta \cdot 10^4$	b) p_{H_2O} мм рт. ст.	c) m_{H_2O} мг	d) % вес. H_2O	e) $\tau_{мин}$ мин.	f) τ_{700} мин.
0,0678	65	126	0,774	1,14	100	945
0,1756	196	90	0,754	0,43	90	806
0,2433	204	117	0,764	0,31	67	686
0,5348	547	96	0,963	0,18	54	580
0,9180	927	101	1,38	0,15	46	415
1,2001	1180	117	1,90	0,16	60	306
2,1478	2400	104	2,58	0,12	52	306

a) m_{NG}, g; b) p_{H_2O}, mm Hg; c) m_{H_2O}, mg; d) % by weight H_2O;
e) τ_{min}, minutes; f) τ_{700}, minutes.

The above refers to comparatively large degrees of filling (0.006–0.2). At small δ (order of 0.001) a significant part of the water (more than 95%) is in the gas phase. In these conditions we did not observe the characteristic picture of decomposition of NG in the presence of water (period of constancy of pressure, fall and its accelerated growth) in a range of initial pressures of its steam from 10 to 300 mm Hg.

The data from these experiments are given in table 3.

Table 3

Decomposition of NG in the presence of water at 100° and small δ

$m_{НГ}$, г a)	$\delta \cdot 10^4$	p_{H_2O} мм рт. ст. b)	% вес. H_2O c)	$\left(\frac{\Delta V}{\Delta \tau}\right)_{нач}$ d)	$\left(\frac{\Delta V}{\Delta \tau}\right)_{макс}$ e)	$\tau_{макс}$ мин. f)
0,0112	12	0	0	0,0069	0,027	[illegible]
0,0198	19	11	0,26	0,0086	0,100	22 600
0,0123	17	40	1,12	0,0021	0,010	35 600
0,0141	20	318	8,02	0,0025	[illegible]	1 000

Conditional designations:

$\left(\frac{\Delta V}{\Delta \tau}\right)_{init.}$ initial — initial speed of gas formation in n cm^3/g min;

$\left(\frac{\Delta V}{\Delta \tau}\right)_{max}$ — speed of gas formation on maximum in n cm^3/g min;

τ_{max} — time of achievement of maximum speed in minutes.

a) m_{NG}, g; b) p_{H_2O}, mm Hg; c) % by weight H_2O; d) $\left(\frac{\Delta V}{\Delta \tau}\right)_{initial}$;

e) $\left(\frac{\Delta V}{\Delta \tau}\right)$ max; f) τ_{max}, minutes

In the decomposition of anhydrous NG at 100° and δ = 0.0012, pressure at first quickly grows, and then, after the speed attained maximum, changes on a curve of the saturating type (fig. 19, curve 1). Such a dependence of change of pressure on time was observed in decomposition of NG in the presence of small quantities of water (p_{H_2O} = 10-40 mm Hg, 0.3-1.1% by weight). However, as can be seen from fig. 20, the magnitude of maximum speed of gas formation and time of its achievement are excellent. Water in a quantity of 0.28% by weight (p_{H_2O} = 11 mm Hg) increased maximum speed as compared to anhydrous nitro esters by more than 3.5 times, and in a quantity of 1.12% by weight (p_{H_2O} = 40 mm Hg) decreases it by approximately three times (cf. fig. 20, curves 1, 2, 3).

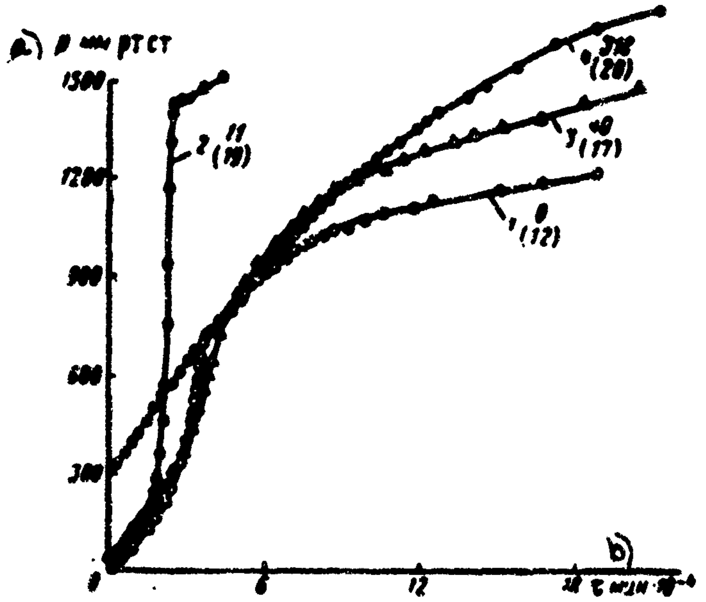

Fig. 19. Change of pressure in decomposition of NG in the presence of water at 100° and small δ.

Numbers by curves— ordinal number of curve, equilibrium pressure of water vapor and $\delta \cdot 10^4$ (in parentheses). a) p mm Hg; b) τ minutes.

In the first case, maximum speed of gas formation almost by 40 times exceeds the initial speed, while in the second -by 5 times.

An increase of the quantity of water to 8% by weight (p_{H_2O} = 318 mm Hg) changes the form of curve $P = f(\tau)$: in the beginning, pressure for certain time is insignificantly lowered, after which it increases at first with slight acceleration, and then by a saturating curve (see fig. 19, curve 4). In fig. 20 (curve 4) it is clear that the maximum speed of gas formation by 40% exceeds the initial speed and is almost by 3 times less than the maximum disintegration rate of anhydrous NG. It is characteristic that in this case during the entire experiment a brown color was not observed in the gas phase. In the preceding experiments the gas phase, in the beginning is colorless, gradually turned brown (NO_2), and then, after achievement of maximum speed of gas formation, the color disappeared.

From this series of experiments it is clear that there exists the most effective quantity of water, causing earlier and stronger acceleration of gas formation; with a greater content of it, the delaying influence should be mentioned, and a sufficiently large quantity of H_2O delays disintegration so much that the even character of dependence $P = f(\tau)$ changes.

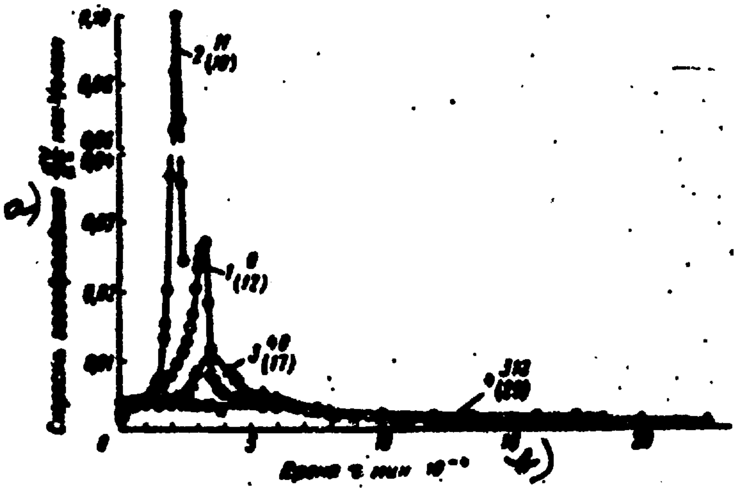

Fig. 20. Change of speed of gas formation in decomposition of NG in the presence of water at 100° and small Δ.

Numbers by curves—ordinal number of curve, equilibrium pressure of water vapor and Δ (in parentheses).

a) Speed of gas formation $\frac{dV}{d\tau}$ a $cm^3/g \cdot min$; b) Time τ minutes.

Influence of Preliminary Heating of Nitroglycerine on its Subsequent Decomposition in the Presence of Water

It was possible to assume that accumulation of acid in a determined concentration leads to fast, probably hydrolytic, development of a reaction, which is developed in the form of a fall of pressure. In the decomposition of anhydrous NG on the initial stages will be formed acid products, but hydrolysis does not occur due to the shortage of water. If however to such, preliminarily decomposed NG, one adds water, then there should immediately start a fast hydrolytic reaction, since both conditions were fulfilled, necessary for its fast flow- the presence of acid, formed by thermal disintegration, and water. If this idea was correct, then, upon adding water to partially decomposed anhydrous NG, it was possible to expect an immediate fall of pressure and subsequent accelerated gas formation.

Anhydrous NG at first was heated at 80° 980 minutes i.e., for a duration of time corresponding to the duration of the induction period, observed in the presence of water. Then in the reaction vessel water was introduced ($p_{H_2O} \approx 180$ mm Hg), and NG was again heated at that same temperature.

Data of this and analogous experiments are shown in table 4.

Table 4

Influence of preliminary heating on decomposition of nitroglycerine in the presence of water at 80 and 100°.

t°C	$m_{НГ}$ г a)	$k\cdot10^6$	τ мин. b)	p_{H_2O} мм рт. ст. c)	% вес. H_2O d)	τ_{min} мин. b)	τ_{700} мин. b)
80	0,3148	354	—	188	0,63	900	1735
	0,2993	338	980	181	0,62	980	1609
	0,3320	369	980*	~200	~0,65	200	650
100	0,2850	336	—	157	0,38	66	390
	0,3970	327	180	135	0,33	45	270

τ - Time of preliminary heating of NG.

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* Heating was conducted in the presence of a small (~ 4 mm Hg) quantity of water.

a) m_{NG}, grams; b) τ min; c) mm Hg; d) % by weight.

So that there occurred/ a fall of pressure and further development of the reaction, 850 minutes was demanded (fig. 21, curve 2), while for preliminary not decomposed nitro esters - 750 minutes (curve 1).

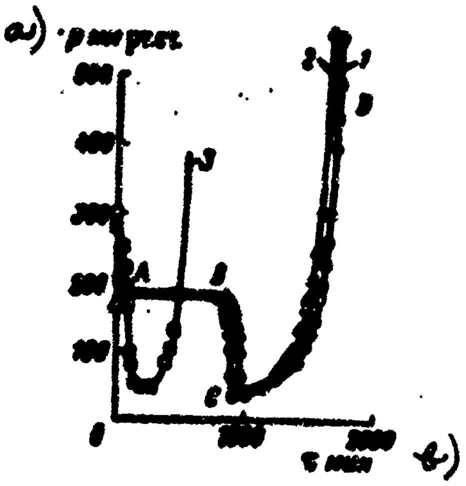

Fig. 21. Influence of preliminary heating of NG on its decomposition in the presence of water at 80°.

1- without preliminary heating, p_{H_2O} = 188 mm Hg, δ = 0.0354; 2- heating at 80° 980 minutes, p_{H_2O} = 181 mm Hg, δ = 0.0338; 3- heating at 80° 960 minutes in the presence of water (p_{H_2O} ~4 mm Hg), p_{H_2O} = 200 mm Hg, δ = 0.0389.

a) p, mm Hg; b) Time, minutes.

Thus, preliminary decomposition of anhydrous NG did not render an essential influence on the rates of development of the reaction in the presence of water.

This indicates that either in anhydrous disintegration the formation of products, stimulating hydrolysis, proceeds much more slowly than in the presence of water, or that in it will be formed other products, or both factors play a role. In order to explain this, experiments were conducted with longer preliminary heating of anhydrous NG, and also experiments with portion introduction of water. Anhydrous NG was heated at 100° for the duration of 180 minutes. Upon continuation of the experiment with added water, τ_{min} was reduced by 20 minutes, i.e., approximately by 30%. Thus, the acid products stimulatingly hydrolysis, will also be formed in the decomposition of anhydrous NG, but significantly slower than in the presence of water.

In another series of experiments, preliminary heating was conducted in the presence of minute (equilibrium pressure approximately 4 mm Hg) quantities of water.

With the subsequent introduction of large quantities of the latter, there immediately began a fall of pressure; after 200 minutes it stopped, and fast acceleration of gas formation was developed (fig. 21, curve 3). This indicates that sufficiently very small quantities of some intermediate acid products formed in the decomposition of NG in the presence of water, in order to initiate a reaction of combining water and the subsequent sharp acceleration of decomposition of nitro esters. Thus preliminary heating in the presence of water especially with its portion introduction, much stronger stimulates decomposition of NG, than "waterless" heating.

Change of Acid Content in a Reaction Vessel in the Decomposition of Nitroglycerine in the Presence of Water [1]

If in the presence of water there occurs hydrolytic decomposition of NG, then acid must be formed. These acids can render catalytical action on the process. Therefore it was expedient to determine the change of acidity in the course of decomposition and the acid, by which it was stipulated.

The most probable is formation of nitric and nitrous acids in the decomposition of NG in the presence of water. Nitric acid can be formed first, in hydrolysis of NG in the usual way, and, secondly, as a result of the interaction of nitrogen peroxide with water formed during thermal disintegration of NG. In the last case nitrous acid will be formed also. Another source of nitrous acid can be the hydrolytic reaction of nitro esters, analogous to the reaction of ^{E}co, observed by Baker [6], [7] in alkaline hydrolysis of certain alkylmononitrates, in which there will be formed a carbonyl compound and ion NO_2^-. Nitrous acid can be formed also in the reduction of nitric acid.

In order to establish which reaction predominates on the initial (up to p_{min}) stage of decomposition, experiments were conducted on detection and quantitative determination of ions NO_2^- and NO_2^-.

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[1] This series of experiments was conducted by student N. V. Gul'tsev.

For determination ion NO_2^- in products of decomposition, was decomposed in the presence of water at 100° $\delta = 0.08998$, $p_{H_2O} = 105$ mm Hg, $p_{min} = 34$ mm Hg after 50 minutes in a reaction vessel, fastened to a diaphragm manometer through a tube with a thin intake. Upon achievement of p_{min} the diaphragm device was removed from the thermostat, the reaction vessel was cooled by liquid nitrogen in order to preserve in it all gases condensed at the boiling point of liquid nitrogen [1], after which the intake was resealed. An ampoule with NG and with the condensed products of decomposition was uncovered under a solution of 0.1 n. alkali, and the whole volume of the ampoule was filled with this solution, which indicated the dissolution in it of all gas products. The solution was quickly separated from the NG. It bleached potassium permanganate in an acid medium, yielded a weakly colored brown ring with ferrous sulfate in the presence of diluted sulphuric acid and separated iodine from a solution of potassium iodine in an acid medium. Nitro esters of such reactions were not yielded. This served as proof of the presence of ions NO_2^- in the obtained alkaline solution; judging by the small intensity of the shown reactions, it may be concluded, that the quantity of NO_2^- -ions was small.

The presence of nitric acid was judged by the formation of a deposit which appears in pouring a nitron reagent into the investigated solution acidified by sulfhuric acid (10% solution of dihydro-diphenyl-phenylimino-triazol in 5% acetic acid) /11/, and nitrous acid before determination was decomposed by a solid hydrazine sulfate.

The relationship between nitric and nitrous acid was determined both in gas products of decomposition and also in products of decomposition, dissolved in an aqueous alkali solution. In both cases the sample for analysis was removed in the moment corresponding to p_{min}, which is a sharp boundary between two macroscopic stages of the process of decomposition of moist NG. In the first case the gas

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[1] It turned out that all gas formed on this stage of disintegration are completely condensed at the temperature of boiling of liquid nitrogen.

products of decomposition of nitroglycerine were collected in a U-tube cooled by liquid nitrogen [1], which then was uncovered under a determined (15 or 25 ml) quantity of 0.1 n solution of NaOH. The solution obtained in this manner was analyzed on nitric and nitrous acid. In the second case, the gas products gathered in the reaction vessel upon its cooling with liquid nitrogen. This vessel then was unsealed from the diaphragm manometer and uncovered under a determined quantity of 0.1 n solution of NaOH; then division of NG was accomplished. Further operations were the same in both cases.

Analysis was conducted with the help of a reagent of nitron by the method described by Busch [8]. By this method, in a separate test the nitrite was oxidized by hydrogen peroxide to a nitrate which jointly with the nitrate already existing in the solution was precipitated in the form of a nitrate-nitron; in another separate test the nitrite was destroyed by hydrazine sulfate, and the remaining nitrate was precipitated by the nitron.

The following example is typical for the determination of the relationship of nitric and nitrous acids, formed at the moment of passage of pressure through minimum. Nitroglycerine in a quantity of 3.436 g was decomposed in a reaction vessel with a diaphragm manometer 23.0 cm^3 in volume in the presence of water vapors (p_{H_2O} = 367 mm Hg). After 55 minutes at p_{min} = 78 mm Hg, all gas products were transferred to the lower part of the reaction vessel, cooled by liquid nitrogen, after which the vessel was unsealed from the diaphragm manometer and was uncovered under 25 ml of a 0.1 n solution of NaOH. 5 ml was removed from the solution obtained in this manner in such a way as not to seize the undecomposed NG. After acidification by sulphuric acid into it was poured 2 cm^3 of 3% solution of hydrogen peroxide. The solution was heated to 70°; though a pipette, 2 cm^3 of a 3% of H_2SO was introduced into it and heated to 90°. Into the solution prepared in this manner, 1.2 cm^3

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[1] Methodology of sampling of gas products is described below.

of the reagent nitron was added. The solution with falling deposit was cooled by ice water, the deposit was filtered and washed on a filter with a small quantity of ice water. The weight of the obtained deposit was 0.0605 g.

$$\%(HNO_3 + HNO_2) = \frac{5,6 \cdot 0,0605 \cdot 0,1679 \cdot 100}{3,4062} =$$

1.45% by weight with respect to NG.

The second 5 ml of the solution, neutralized by 2n sulfuric acid, was evaporated to 1 ml and was added by drops to 0.05 g dry hydrazine sulfate, after which the nitrate existing in the test was precipitated as it was described above. The weight of the obtained precipitate was 0.058 g.

$$\%(HNO_3) = \frac{5,6 \cdot 0,058 \cdot 0,1679 \cdot 100}{3,4062}$$ = 1.39% by weight with respect to NG.

Initial data and results of this experiment and three others are given in table 5.

Table 5

Determination of nitric and nitrous acid in the decomposition of nitroglycerine at 100° in a moment corresponding to p_{min}.

$m_{НГЦ}$ г a)	$\delta \cdot 10^4$	p_{H_2O} мм рт. ст. b)	τ_{min} мин. c)	p_{min} мм рт. ст. b)	% вес. (HNO_3+HNO_2) по отношению к НГЦ d)	% вес. HNO_3 по отношению к НГЦ d)
3,406	865	367	55	78	1,45	1,39
2,120	784	286	58	70	2,16	2,12
2,140	815	480	47	113	1,79	1,76
2,064	809	430	55	95	1,87	1,82

a) ^{m}NG, grams; b) mm Hg; c) τ minutes; d) % by weight with respect to NG.

In the first two experiments, nitric and nitrous acid were determined by the above-described methodology. In the last two, the gas products of disintegration at first were collected in a U-tube, and then were analyzed.

In spite of the comparatively small accuracy of determination (since in the experiments a small quantity of NG was used, the solubility of products of disintegration in nitro esters in determination by the first method was not considered and complete extraction of gas products during the analytic work by the second method was not guaranteed, it is plainly evident that the quantity of nitrous acid constitutes an insignificant part of total acidity (not more than 4%).

Thus, the main product of acid character, formed at the moment corresponding to p_{min}, is nitric acid. Its formation can be naturally explained by hydrolysis of NG of the normal type, as a result of which will be formed ions NO_3^- and a hydroxyl group for an atom of carbon. This is in accordance with the data of Farmer [2], who detected, in hydrolysis of NG with diluted nitric acid, glycerine dinitrate. The detected small quantities of nitrous acid, as it was shown above, can be formed, first, in decomposition and reduction of the yielding nitric acid, and, secondly, in the dissolution of nitrogen peroxide in water, split from NG as a result of thermal disintegration [1], and finally, due to the passage of a hydrolytic reaction of the type E_{co}, yielding ion NO_2^- and a carbonyl compound. However, if all these reactions occur, then it will be in a very small degree.

The predominant presence of nitric acid in the reaction vessel on the stage of disintegration of NG up to p_{min} allowed later to determine the quantity of acid by titrating with alkali a solution obtained by processing the gas products of disintegration by water, taking all the acid formed to be nitric. For that, decomposition of NG in the presence of water was conducted in a reaction vessel joined to a diaphragm manometer through a tube with intake. In a determined stage of decomposition the diaphragm device was removed from the thermostat; after the gas products by cooling with liquid nitrogen were transferred to the lower part of the

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[1] According to the data of N. V. Gul'tsev in the decomposition of anhydrous NG at 100° towards 130 minutes in the reaction vessel was found by titrating 0.13% (in recount on HNO_3 acid, or ~ 0.04% to the moment of time, corresponding to p_{min}. This is in satisfactory agreement with the data on the analysis of nitrous acid, formed during decomposition of NG in the presence of water (see table 5).

reaction vessel , the intake was resealed. An ampoule with NG and products of decomposition was uncovered under water [1]. The solution obtained was titrated by a 0.01 n solution of NaOH (indicator-phenolphtalein). In the calculation it was assumed that all acidity is conditioned by nitric acid.

Determination of acidity was conducted in two stages of decomposition of NG in the presence of different quantities of water at 100° and $\delta = 0.03-0.04$: in the beginning of the fall of pressure (in the end of the induction period) and at p_{min}. Initial data and results of these experiments are in tables 6, 7 and 8.

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[1] For removal of carbon dioxide, the water was preliminarily boiled.

Table 6

Acidity in the end of the induction period of decomposition of nitroglycerine in the presence of different quantities of water at 100°

a) $m_{НГЦ}$ г	$a \cdot 10^4$	b) p_{H_2O} мм рт. ст.	c) % вес. H_2O	b) p мм рт. ст.	d) τ мин.	e) % вес. HNO_3 по отношению к НГЦ	$\frac{\% HNO_3}{p_{H_2O}\tau} \cdot 10^6$
0,3259	315	71	0,18	67	37	0,11	42
0,2716	319	88	0,22	78	55	0,17	35
0,3314	318	195	0,48	182	60	0,28	24
0,3666	324	222	0,54	214	43	0,22	23
0,2960	311	238	0,60	223	130	0,60	19,5
0,3041	313	267	0,64	254	90	0,48	20
0,3884	382	294	0,65	286	41,5	0,21	17,2
0,3276	314	363	0,91	360	48	0,20	11,5
0,3164	282	408	1,09	389,5	62	0,22	8,7
0,3091	333	406	0,98	387	61	0,22	8,9

τ -Time in minutes of achievement of pressure p, with which acidity was determined.

(a) m_{NG}, grams; (b) mm Hg; (c) % by weight; (d) Minutes; (e) % by weight-with respect to NG.

Table 7

Acidity in a moment, corresponding to p_{min}, in the decomposition of nitroglycerine in the presence of different quantities of water at 100°

a) $m_{НГЦ}$ г	$a \cdot 10^4$	b) p_{H_2O} мм рт. ст.	c) % вес. H_2O	b) p_{min} мм рт. ст.	d) τ_{min} мин.	e) % вес. HNO_3 по отношению к НГЦ
0,3259	375	52	0,11	29	64	0,58
0,3684	404	146	0,31	49	60	1,41
0,3215	333	172	0,41	57	58	1,62
0,2837	330	222,5	0,54	62	72	2,21
0,3153	346	262,5	0,62	83	121	2,32
0,3110	370	316	0,72	82,5	78	2,74
0,4055	396	375	0,82	90	69	2,93
0,3346	364	375	0,86	89	87	2,94
0,2896	279	396	1,07	101,5	106	4,37
0,3070	333	510	1,23	136	103	4,74
0,3988	496	520	1,02	116	84	3,70

(a) m_{NG}, grams; (b) mm Hg; (c) % by weight; (d) minutes; (e) % by weight-with respect to NG.

Table 8

Dependence on δ of acidity in a moment of time corresponding to p_{min}, in the decomposition of nitroglycerine in the presence of an approximately constant quantity of water at 100°.

a) $m_{НГЦ}$ г	$\delta \cdot 10^4$	b) p_{H_2O} мм рт. ст.	c) m_{H_2O} мг	d) % вес. H_2O	b) p_{min} мм рт. ст.	e) τ_{min} мин.	f) % вес. HNO_3 по отношению к НГЦ
0,0780	82;2	286	1,42	1,82	106,5	160	5,98
0,1736	201	250	1,44	0,84	76	100	2,02
0,2679	202	226	2,04	0,76	76	72	2,57
0,3153	346	263	1,85	0,62	83	121	2,32
1,0034	870	298	4,52	0,45	82	55	1,20
2,0794	1714	252	6,46	0.31	59	53	1,66

(a) m_{NG}, grams; (b) mm Hg; (c) mg; (d) % by weight; (e) minutes; (f) % by weight - with respect to NG.

From a comparison of tables 6, 7 and 8 it is clear that the fall of pressure is accompanied by a sharp increase of acidity. Acidity in the beginning of the fall of pressure little depends on the initial quantity of water in the reaction vessel and constitutes ~0.2%. Only in those experiments, where the induction period is more than usual, this magnitude is somewhat increased. The quantity of acid, determined in a moment, corresponding to p_{min}, depends on the intial quantity of water in the reaction vessel; the larger it is, the bigger the contents of acid.

As it was shown above, an increase of δ at constant initial pressure of water vapors signifies a decrease of the quantity of H_2O in the reaction vessel. Determination of acidity in moment p_{min} at various δ and pH_2O = 230 - 290 mm Hg showed that an increase of δ also decreases the quantity of formed acid (see table 8). In fig. 22 are the results of experiments in determining acidity in a moment, corresponding to p_{min}, in the decomposition of NG in the presence of different quantities of water and at different δ. The dependence of the change of contents of acid on the quantity of water is depicted by a straight line with tangent of the angle of inclination, approximately equal to 3.6, which is near the ratio of molecular scales of nitric acid and water $\frac{M_{HNO_3}}{M_{H_2O}}$ 3.5. Equimolecular ratio of water, existing in the beginning, and nitric acid, formed at a moment, corresponding to p_{min}, and also the absence of any other acids in significant quantities, provides enough weighty proof that in the decomposition of NG in the presence of water there occurs hydrolysis of the usual type with the formation of nitric acid.

If one were to allow that as a result of the interaction with water, one nitrate group in NG is converted into alcohol with the formation of nitric acid and glycerine dinitrate[1], then it turns out that in the presence of 1% water (pH_2O = 400 mm Hg) at $\delta \approx 0.03$, 3.5% by weight nitric acid will be formed. This means that at the moment, corresponding to p_{min}, approximately 13% by weight of the initial quantity of NG was decomposed. Decomposition of such a quantity of nitro esters occurs in a very short range of time: the time of the fall of pressure consitiutes at 100° and $\delta \approx$ 0.03. 35-45 minutes. This fall, occurring at first with small, but increasing speed, after its passage through the maximum, is slowed down; then, the greater the initial pressure of water vapors, the greater the

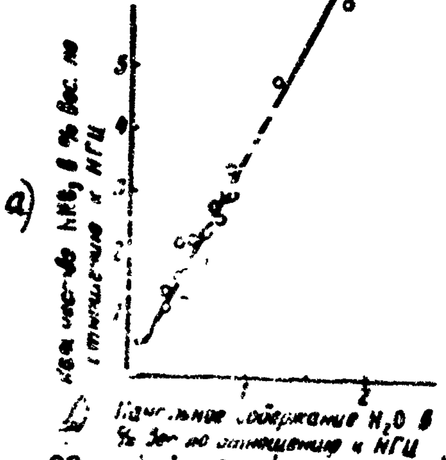

Fig. 22. Acidity in a moment corresponding to p_{min} in the decomposition of NG in the presence of different initial quantities of water at 100°. (a) Quanitity of HNO_3 in % by weight in reference to NG; (b) Initial contents of H_2O in % by weight in reference to NG.

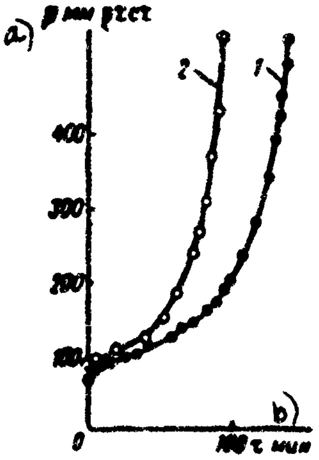

Fig. 23. Decomposition of NG in the presence of nitric acid and glycerine dinitrate at 100°.
1) NG + 8.6% by weight DNG + 4.9% by weight HNO_3, = 0.0448;
2) NG + 1.04% by weight H_2O, δ = 0.0305.
a) p mm Hg; b) time, minutes

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[1] Simultaneously with this reaction hydrolysis of the formed dinitrate glycerine can occur; however due to its smaller concentration as compared with the concentration of NG, the first reaction, probably is predominant.

maximum speed of fall of pressure.

The fast increase of speed of fall of pressure indicates an autocatalytic process: the nitric acid being yielded speeds up the reaction of the interaction of NG and water. By measure of expending the water, the fall of pressure is delayed. Possibly, the autocatalytic reaction occurs also for the duration of the induction period. However, for proof of this it is necessary to study the kinetics of the change of acidity in this section of decomposition.

Nitric acid, formed as a result of the autocatalytic reaction of hydrolysis of NG and water, apparently, causes further development of the process of transformation, developed in accelerated gas formation.

If this conclusion is correct, then after addition to NG of glycerine dinitrate and nitric acid, accelerated growth of pressure must immediately start, analogous to that which is observed after the passage of pressure through the minimum in the decomposition of NG in the presence of water. Indeed, NG (δ = 0.0448) in the presence of (above 100) 4.9% by weight nitric acid and 8.6% by weight symmetric glycerine dinitrate immediately starts to be rapidly decomposed (fig. 23, curve 1).

In this figure for comparison is depicted a curve 2 of the change of pressure in time in the decomposition of NG in the presence of 1% by weight water. In this case during hydrolysis of NG 3.5% by weight nitric acid and ~10% weight glycerine dinitrate should be formed. To more graphically compare both experiments, after the beginning of reading of time a moment was selected, corresponding to P_{min}.

The Role of Volatile And Nonvolatile Products

In the decomposition of NG in the presence of moderate quantities of water, after the induction period and the fall of pressure following it, occurs a more or less accelerated gas formation. The fall of pressure is accompanied by a significant increase of the contents of volatile acid in the reaction vessel, formed as a result of the interaction of NG with water. It turned out that this basically is nitric acid. Possibly, it also is a cause of subsequent accelerated decomposition, accompanied by strong gas formation. Probably, simultaneously with the separation of acid nonvolatile products of reactions will also be formed, containing group OH (in particular, glycerine dinitrate), which can participate in the future development of the process. In order to explain what role is played by the gas and condensed products in the decomposition of moist NG after passage of pressure through the minimum, the following experiments were set up.[1]

First, from NG decomposing in the presence of water, in a moment, corresponding to p_{min}, the volatile products were evacuated, after which it was heated again.

Secondly, the NG, from which the volatile products of desintegration formed at the moment corresponding to p_{min}, after preliminary decomposition were removed, and were decomposed again in the presence of the introduced water vapors.

Third, anhydrous NG was decomposed in the presence of volatile products of disintegration.

For the execution of these experiments NG at first was decomposed in the presence of water in a reaction vessel, united through a tube (with an intake for facilitating unsealing) with a vacuum cock of special design[2] (fig. 24). The cock was smeared with a thermoresistant low-reactive lubricant, prepared from perfluorinated hydrocarbons; for the best hermetic sealing the top of the stopper of the cock was flooded by mercury (mercury sealing). Due to this, the instrument could be submerged into a thermostat liquid in such a manner, that the entire reaction container was at the temperature of the experiment. During the experiment the cock was closed. In that moment, when it was necessary to pump the gases, the instrument was removed from the thermostat and joined to a vacuum installation. For fasterand more complete removal of gases, NG periodically

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[1] These experiments were conducted by N. V. Gul'tsev, a student.

[2] The same cock was used in the introductions of leads to decomposing NG and in pumping the volatile products of decomposition from it (see p. 213).

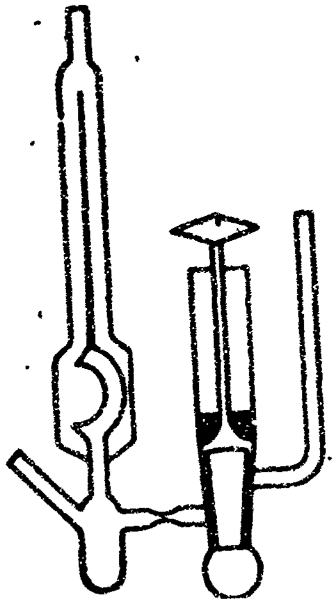

Fig. 24. Reaction vessel with cock of special design for removal of volatile products of decomposition

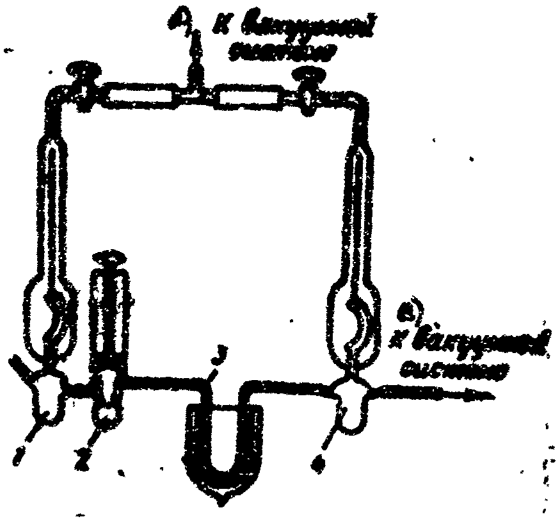

Fig. 25. Diagram of installation for removal of volatile products of decomposition from reaction vessel with NG. 1 and 4 - reaction vessels, 2 - vacuum cock, 3 - U-tube.
(a) To vacuum system.

was heated to $\sim 40°$, and the trap on the vacuum installation was filled with liquid nitrogen. To completely remove the volatile products of decomposition from NG is difficult: it is necessary, so that the nitro esters at least for twenty-four hours are under a vacuum. Usually under a vacuum NG was maintained for two days. After removal of volatile products of disintegration, the intake, connecting the reaction vessel with the cocks, was resealed. If it was necessary, before this operation water vapors were introduced into the reaction vessel by the usual method.

In the preparation of the experiment on decomposition of anhydrous NG in the presence of products of disintegration the following method was applied (fig. 25). Moist NG was decomposed in a reaction vessel 1, united with cock 2, described above. After interruption of decomposition, this part of the design of the instrument was sealed through the U-tube 3 to the reaction vessel 4 with a diaphragm manometer and a weighed amount of anhydrous NG. Vessel 4, in turn, was joined to the vacuum installation. After evacuation of this part of the system, cock 2 was opened and the volatile products of decomposition from vessel 1 were collected in U-tube 3, cooled by liquid nitrogen. The volatile products collected in it were transferred to reaction vessel 4 by means of cooling it with liquid nitrogen; then the U-tube 3 was heated to room temperature.

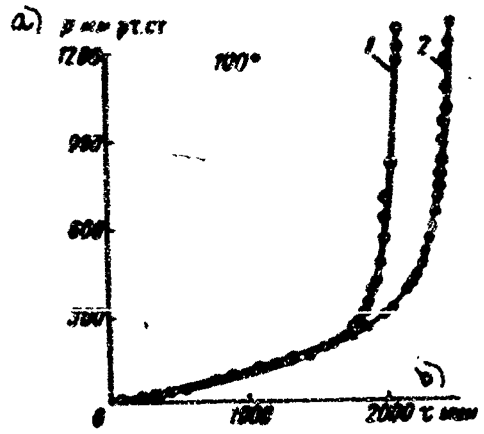

Fig. 26. Disintegration of NG preliminarily decomposed in the presence of water and liberated from volatile products of decomposition.
1- NG preliminary decomposed in the presence of water, $\delta = 0.0328$; 2 - NG not subjected to preliminary decomposition, $\delta = 0.0329$.
(a) p mm Hg; (b) time, minutes.

The results of the experiments are such. NG at first was decomposed in the presence of water ($pH_2O = 198$ mm Hg) at 100° and $\delta = 0.0277$. After the fall of pressure usual in these conditions and the achievement after 68 minutes of its minimum value (71 mm Hg) all volatile products were thoroughly pumped, as described above. The nitro esters obtained in this manner, possibly containing low-volatile products of disintegration formed as a result of its preliminary decomposition in the presence of water, were subjected to further decomposition at 100° and $\delta = 0.0328$.

It turned out that in this case the general character of the dependence $p = f(\tau)$ is the same as in the decomposition of anhydrous NG, not subjected to preliminary decomposion (fig. 26). Their initial speeds of gas formation are approximately equal, however, acceleration of disintegration in NG, preliminary subjected to decomposition in the presence of water, began 7 hours earlier, which constitutes nearly 15% of the time to the beginning of sharp acceleration of gas formation in the decomposition of anhydrous NG.

If after removal of volatile products from NG, formed in it as a result of preliminary decomposition in the presence of water, H_2O vapors are added to it and secondarily subjected it to heating, a picture will be observed which is ordinary under these conditions: the induction period, fall of pressure and its accelerated growth (fig. 27, curves 1 and 3). The duration of the induction period remains approximately the same (curve 1) or is somewhat increased (curve 3), however the subsequent accelerated growth of pressure occurs in these experiments a little earlier in comparison with NG not subjected to preliminary decomposition (curve 2).

From these experiments it follows that the low-volatile products of interaction on NG and water forming at the moment, corresponding to p_{min}, do not exhibit almost any action on the initial stage of subsequent decomposition both of moist and also anhydrous NG, but, as it was shown above, sharp acceleration of gas formation in preliminarily decomposed NG occurs a little earlier.

What has been mentioned is correct only with the condition of complete removal of volatile products of disintegration after preliminary decomposition. If however, they are not completely removed (preliminarily decomposed NG was under vacuum for 12 hours, instead of 48, as usual), then the induction period for such NG was practically absent; the pressure, having reached its maximum (due to evaporation of water vapors during warm-up), immediately began to fall and after 27 minutes crossed the minimum (fig. 27, curve 5).

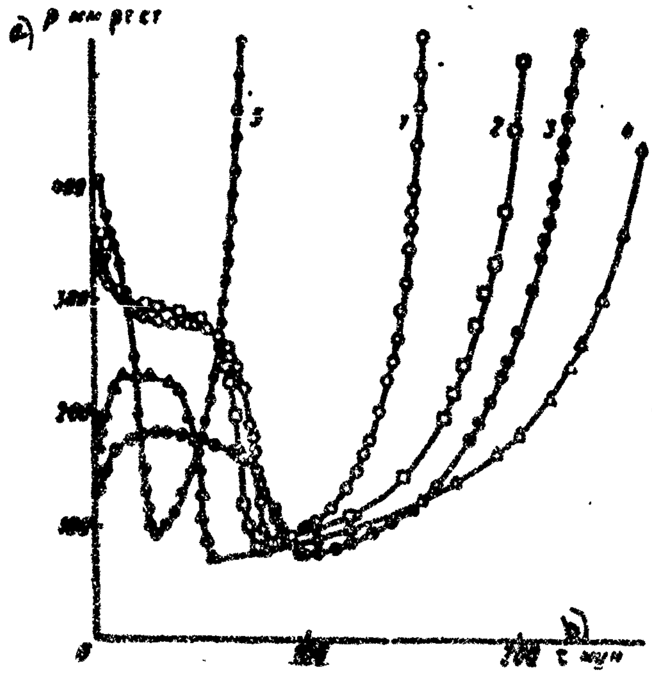

Fig. 27. Influence of nonvolatile products of disintegration of moist NG on repeated decomposition of it in the presence of water at 100°. 1) NG, preliminarily decomposed, p H_2O = 278 mm Hg, $\delta = 0.0354$; 2) NG, not preliminarily decomposed, p H_2O = 293 mm of Hg, $\delta = 0.0367$; 3) NG, preliminarily decomposed, p H_2O = 182 Hg, $\delta = 0.0355$; 4) NG, not preliminarily decomposed, p H_2O = 230 mm Hg, δ = 0.@ 03223; 5) NG, preliminarily decomposed upon incomplete removal of products of decomposition before repeated heating, p H_2O = 355 mm Hg, $\delta = 0.0459$. (a) p mm Hg; (b) Time, minutes.

Subsequent gas formation was continued with great speed and at the 80th minute was sharply accelerated.

If the development of the process, occurring after the fall of pressure, was influenced only by the gas products of decomposition, and the formed nonvolatile substances did not render any influence on it, then the course of disintegration of pure NG in the presence of volatile products of decomposition, formed at a moment, corresponding to p_{min}, and the course of decomposition of moist nitroglycerine after passage of its minimum by pressure should have been identical.

However the experiments show that this is not so. In fig. 28 (curves 3 and 4) is represented the change of pressure in time in the experiment, in which to pure, preliminarily pumped NG, we added volatile products of decomposition of moist nitroglycerine, formed at a moment, corresponding to p_{min}. For comparison, on that graph, curves of decomposition of NG in the presence of water are shown, and after beginning of reading of time, the moment of passage of its minimum value by pressure (curves 1 and 2)is received.

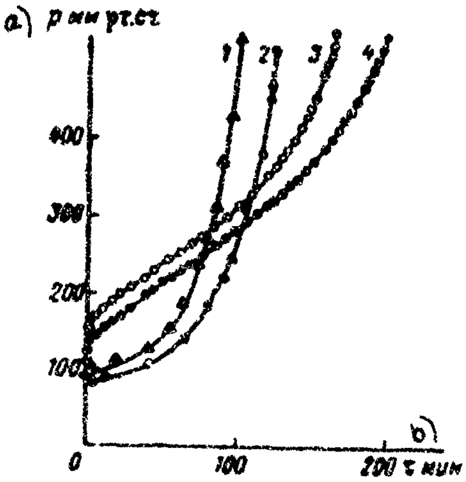

Fig. 28. Influence of volatile products of disintegration of moist NG on its decomposition at 100°. 1) NG $+H_2O$, p H_2O = 408 mm Hg, $\delta = 0.0305$; 2) NG + H_2O, p H_2O = 293 mm Hg, $\delta = 0.0367$; 3) NG + volatile products of decomposition. $\delta = 0.0301$; 4) NG + volatile products of decomposition, $\delta = 0.0356$. (a) pressure, mm Hg;(b) time, minutes.

From the experiments it follows that the gas products of disintegration have a weaker influence on the decomposition of pure NG, than on the decomposition of nitro esters, containing nonvolatile products of decomposition; in the last case, the time up to sharp acceleration of gas formation is reduced approximately twice.

This is in accordance with the preceding series of experiments. In all those cases, when in NG there are nonvolatile products of its decomposition, formed at a moment, corresponding to p_{min}, acceleration of gas formation occurs earlier, than in their absence, i.e. glycerine dinitrate, formed as a result of hydrolysis, is either more subject to oxidising action, or promotes disintegration of NG.

Decomposition of glycerine dinitrate in the presence of water

In connection with the fact that in the decomposition of moist NG as a result of hydrolysis, possibly the formation glycerine dinitrate, which then can enter in reaction with water and with acid, was interesting to study the kinetics of its decomposition in the presence of water. In this part of the work we did not go into detailed and manifold investigation of the disintegration of the dinitrate, and only attempted to establish its main regularities.

The experiments were conducted at $\xi \approx 0.03$ and 100° in the range of initial (equilibrium) pressures of water vapor 60 - 400 mm Hg, i.e. in such conditions[1], in which in the decomposition of moist NG was observed the characteristic manometric picture of disintegration: induction period, fall of pressure and its growth.

The experiments on the decomposition of asymmetric glycerine dinitrate showed the same dependence of the change of pressure in time (fig. 29), as moist NG, However, distinctions were also observed. With an increase of p H_2O the magnitude of the induction period did not increase, as in the case of NG, but was reduced. Thus, at pH_2O = 57 mm Hg, the time of achievement of p_{min} constituted 150 million, at pH_2O = 220 mm Hg, 68 minutes, and at pH_2O = 412 mm Hg, 40 minutes. In the same range of pressures, as can be seen from the graph, in the decomposition of NG in the presence of water, the time of achievement fluctuates between 60 and 75 minutes.

Another essential distinction of disintegration of glycerine dinitrate from disintegration of glycerine trinitrate is the fact that after achievement of p_{min},

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[1] Solubility of water in glycerine dinitrate is greater than in trinitrate; this means that at a given equilibrium pressure of water vapors, its concentration in the dinitrate is greater than in trinitrate.

pressure grows with a high speed. Essential differences between disintegration of symmetric and asymmetric isomers of dinitrate in the presence of water were not observed.

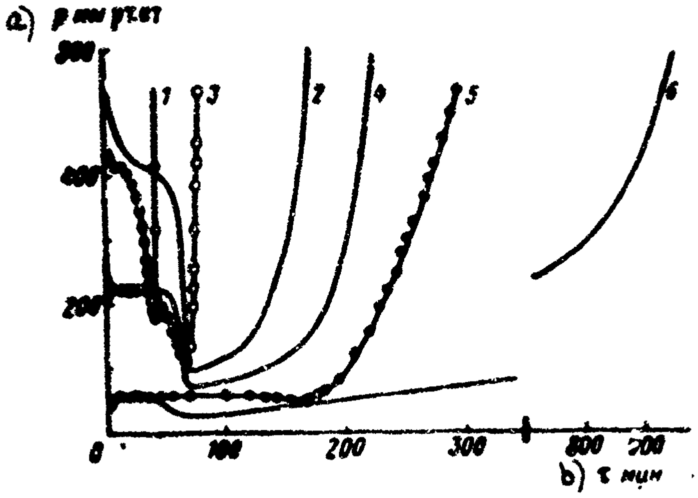

Fig. 29. Decomposition of asymmetric glycerine dinitrate in the presence of water at 100°. 1) DNG + H_2O, p H_2O = 413 mm Hg, δ = 0.0307; 2) NG + H_2O, p H_2O = 408 mm Hg, δ = 0.0305; 3) DNG + H_2O, p H_2O = mm Hg, δ = 0.0251; 4) NG + H_2O, p H_2O = 230 mm Hg. δ = 0.0339; 5) DNG + H_2O, p H_2O=57 mm Hg, δ ≅ 0.03; 6) NG + H_2O, p H_2O = 54 mm Hg, δ = 0.0259
(a) pressure, mm Hg; (b) time, minutes.

The identical character of decomposition of trinitrate and dinitrate of glycerine indicates that in both cases basically occur the same processes. However the distinction in the structure of a molecule (presence of group OH) has a certain influence on the course of decomposition. In particular probably by the presence of the OH group, capable of relatively light oxidation, the high speed of gas formation on the stage of accelerated growth of pressure should be explained.

Discussion of Results

The main causes of acceleration of disintegration of NG, brought about by the gas products of its decomposition, is their oxidizing and hydrolyzing action on the intermediate organic products of disintegration and on nitroglycerine itself.

Admixtures such as water, usually contained nitro esters, and acids, if NG is sufficiently cleansed of the processed acid, can have an analogous influence.

Water causes hydrolysis of NG, leading, as the experiment indicated, to the formation of nitric acid; the speed of hydrolysis naturally is greater, the larger the content of water. However, this speed greatly depends also on the contents of acids in NG, in particular nitric, and this influence can cover the influence of concentration of water in the sense that with a small contents of water, but significant acidity, hydrolysis can proceed much faster, than with a large contents of of water in NG, but in the absence of acid. Diluted nitric acid hardly accelerates hydrolysis; concentrated HNO_3 also. The oxidising action of nitric acid also depends on its concentration; a minimum concentration, starting from which, the development of oxidation is greatly accelerated, is higher than that, with which strong acceleration of hydrolysis occurs.

This leads to an original and different character of the influence of water with various contents of it in the vessel and, in particular, in NG, exhibited in manometric curves in the laboratory experiments.

With small quantities of water, the course of decomposition is similar to that, which is observed for anhydrous NG, but more compressed in time. In coordinates $p = f(\tau)$ it can be represented by the curves in fig. 3 and 4. In the beginning the growth of speed of gas formation proceeds slowly; after achievement of a certain "critical" pressure, the speed grows approximately proportional to the square of total pressure of gas products of disintegration and water.

With average quantities of water the vicissitude of the process is more sharply expressed. Three main stages are clearly distinguished (fig. 21. curve 1):

1) induction period, when pressure (water vapors above NG) remains practically constant (AB);

2) period of fast fall of pressure (BC);

3) period of accelerated growth of pressure (CD).

In the induction period there occurs accumulation of nitric acid in NG as a result of "waterless" disintegration and interaction of its products with water, and also as a result of hydrolisis, slow in the beginning and accelerated by accumulation of acid.

In the second period, starting, when the content of acid reaches several tenths of a percent, water vapors cross into liquid NG and simultaneously as a result of hydrolysis will form nitric acid. Its solubility in nitro esters is much greater than water. This is also determined basically by the relationship of pressures before and after the fall. The concentration of nitric acid in NG at moment of completion of the fall of pressure is several times (depending upon the quantity of water, in the vessel) greater, than it was in the beginning of the period of fall of pressure. Correspondingly, concentration of the organic products of hydrolysis also increases.

In the third period, due to the high concentration of nitric acid, and also the lighter, than NG, oxidised products of hydrolysis, the main role is taken by the oxidising-reduction processes, accompanied by abundant formation gases, both brown and condensed, and also noncondensing (at room temperature). The process is developed faster, the greater the nitric acid is on the minimum of pressure. The speed of gas formation in this period is approximately proportional to the square of pressure.

With large quantities of water (fig. 6, curve 8) the pressure above NG changes relatively little, and after a long time, which can even exceed the time up to sharp acceleration in disintegration of anhydrous nitro esters, insignificant lowering of pressure occurs, after which usually follows its fast growth. With very large relative quantities of water, the maximum of the disintegration rate can be even less than in a "dry" process in the same conditions. The main cause of the decrease of acceleration in the last case is, evidently, the excessive dilution by water of nitric acid and other oxidisers, inhibiting the development of oxidation.

Let us consider now in more detail, three types of "aqueous" decomposition. We will start from the second as the most typical.

If NG contains water, then in it proceed two processes - "waterless" decomposition, not connected with the presence of water, and hydrolysis. The speed of both processes in the beginning is small. However, the speed the first of them almost does not grow, and the speed of hydrolysis is increased under the influence of nitric acid, at first formed chiefly as a result of "waterless" disintegration. In the beginning, this growth proceeds slowly, therefore, the duration of the induction period is basically determined by the speed of the "waterless" reaction. In correspondence with this, according to B. S. Svetlov, is the temperature dependence of the induction period. When the quantity of nitric acid reaches 0.2-0.4% by weight of the quantity of NG, hydrolysis is sharply accelerated. The cause of the sharpness of this increase of speed is not established; possibly, a role is played here, in particular, by the increase of solubility of water in NG, leading to its transition from the gas phase into liquid, which in the experiment in the closed container is manifested in a sharp fall of pressure. During this fall practically all water by means of hydrolysis is turned into nitric acid, and the corresponding quantity of NG will form, apparently, a dinitrate.

The strong increase of concentration of nitric acid in a liquid causes oxidation of the organic products of hydrolysis, and also the actual NG; inasmuch as oxidation yields water, to it hydrolysis is joined, supplying in turn "food" for the oxidizing reduction processes.

The products of hydrolysis are oxidised easier than NG itself, as this was confirmed by a number of experiments. Thus in "aqueous" decomposition of glycerine dinitrate the growth of pressure in the third period proceeded, other conditions being equal, significantly faster, than for NG, although nitric acid in this case can be formed less than in "aqueous" disintegration of glycerine trinitrate. Precisely the same experiments with partially hydrolysed NG, liberated by therough evacuation from volatile acids, showed that its period of acceleration of gas formation occurs both in the presence of water, and also in its absence, faster, than for fresh nitro esters. Finally, the volatile products of disintegration, being added to fresh NG, more weakly accelerated gas formation, than this is observed in the third period of disintegration of moist nitroglycerine.

Thus, in the beginning the successive, and then the joint flow of hydrolysis and oxidation leads to the fact that in the presence of water a large and growing disintegration rate of NG is attained faster, than in its absence. Thus at $\delta \approx$ 0.03 and 100° at "waterless" disintegration, this happened after 40 hours, and in the presence of 1.5% by weight water - after 2 hours.

If there is very little water (for example p $H_2O < 30\text{-}50$ mm at 100° and $\delta \approx 0.03$), then the speed of hydrolysis in the beginning is correspondingly small, but since the acid products of waterless disintegration (and also the acid, formed in the development of hydrolysis) are not diluted considerably by water, and such a concentration of acid is quickly attained, with which hydrolysis proceeds with great (relative to the quantity of water) speed. Formation in these conditions of concentrated (inasmuch as there is little water in the vessel, in order to dilute it) nitric acid, and also the organic products of hydrolysis leads to the development of oxidation, slower, however, than with average quantities water, since there is little nitric acid.

Thus, the general movement of this process is obtained similar to the decomposition of anhydrous NG with that only distinction that in the last case the absence of water in the beginning, which will be formed only later as a result of oxidation, delays the development of hydrolysis: in the presence of even a small quantity of water, it starts immediately and soon, due to the significant acidity, proceeds with a comparatively great speed in spite of the fact that there is little water. As a result, the movement of the "pressure-time" curve, inherent NG is maintained, but the process of acceleration of disintegration, connected with accumulation of nitric acid and oxidation caused by it, is developed significantly faster. Thus at p H_2O = 14 mm, the pressure, equal to 700 mm, was attained in the presence of a small quantity of water twice as fast as for anhydrous NG.

If there is very much water, then it dilutes the acids, formed in the "waterless" reaction, and then also in hydrolysis, and the latter therefore proceeds very slowly in the beginning. As result of this, the time to the approach of the third period can increase. Here we obtain an original picture; hydrolysis lags, and the subsequent acceleration of disintegration, on the contrary, is accelerated, since more nitric acid and organic products of hydrolysis will be formed. Depending upon the conditions, both the first, and also the second influence can predominate, i.e. the total time from the beginning of the experiment to the approach of strong acceleration of gas formation can both decrease, and also increase.

A good illustration of these relationships is given in table 6; at identical δ the pressure of water vapors was increased, i.e. its quantity and contents in NG; the induction period of general changed little and the average speed of formation of acid, referred to the concentration of water $\left[\frac{\%HNO_2}{P_{H_2O}^{\tau}}\right]$, with an increase of the latter, decreased. The cause of this was obviously the smaller time-average concentration of acid, formed by "waterless" disintegration, due to which the speed of hydrolysis was lowered. Let us add that a few experiments, conducted with glycerine dinitrate, showed that for it the induction period was reduced with an increase of water pressure. It is possible that in this case the concentration of water plays a large role, and the accelerating action of acid, a smaller one, than in the case of NG.

At large δ, usually a predominant role is played by the reduction of the duration of the third period and total time of development of the process is reduced with an increase of the quantity of water in NG; at small δ, for example ~ 0.006, it is possible to observe also an increased total time with an increase of the contents of water in NG, and it can become even greater, than for anhydrous nitro esters.

These considerations also explain the increased effectiveness of "portion" introduction of water. If a little water is introduced, then the concentration of acid quickly reaches, due to the "waterless" disintegration, such values, with which hydrolysis occurs quickly and forms much acid. With the repeated addition of water, the process of hydrolysis should not start from the neutral beginning and the total time of both heatings to the fall of pressure is reduced as compared with that which is observed if the entire quantity of water is added immediately.

The small influence of preliminary "dry" heating on subsequent decomposition in the presence of water requires additional explanation. It is necessary to allow that in these conditions side by side with the formation of the highest oxides of nitrogen proceeds their reduction[1], probably to NO, and the subsequent addition of water does not lead to the formation of acids. If, however, the highest oxides of nitrogen are formed in the presence of water, then it, interacting with them, immediately yields acid and dilutes them so much that hydrolysis (forming nitric acid) proceeds with significant speed, and oxidation (destroying the highest oxides of nitrogen) is suppressed (we recall that the concentration of nitric acid, strongly accelerating hydrolysis, is much less than the corresponding concentration for oxidation).

Conclusions

1. The presence of water can render a strong influence on the development of disintegration of NG at increased temperatures.

2. With small quantities of water the type of disintegration is maintained , inherent to anhydrous NG, but it proceeds faster.

3. With average quantities of water we observe three periods of disintegration: constancy of pressure (induction period), fall of pressure and growth of pressure. The last period proceeds faster, the more water there is, and this determines the decrease of the total time of disintegration with the increase of the quantity of water.

4. With large quantities of water, disintegration can be strongly delayed, and the maximum of its speed can be less than even for anhydrous NG.

5. All these regularities are explained proceeding from the assumption that the initial stage of disintegration in the presence of water is hydrolysis, in a neutral medium proceeding slowly, but accelerated by the acid products of the "anhydrous"

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[1] In favor of this assumption, as our attention was turned to this by B. S. Svetlov, is also the reduction of the time to the approach of sharp acceleration in the disintegration anhydrous NG in the presence of oxygen; apparently, oxygen, quickly oxidising NO, decreases the role of the reduction processes, leading to the decrease of concentration of the highest oxides of nitrogen. In exactly the same way, in the case of thermal disintegration of diglycoldinitrate, where the highest oxides of nitrogen are reduced and cannot form acid, the presence of water does not lead to acceleration of disintegration.

reaction and the actual hydrolysis. Hydrolysis leads to the accumulation of concentrated nitric acid and organic products, which cause oxidation, associated with hydrolysis and accompanied by liberation of a large quantity of gaseous products.

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Chapter 2 Article 10

Pages 172-183

K. K. Andreyev and G. N. Bespalov

10. On the Influence of Acids and Soda on the Disintegration of Nitroglycerine in the Presence of Water

Investigation of the decomposition of nitroglycerine (NG) in the presence of water, the results of which are considered in the preceding article, led to the conclusion that an essential stage of disintegration is represented by hydrolysis of NG. This hydrolysis, in the case of neutral nitroether proceeding very slowly, can very greatly be accelerated, if there is created significant concentration of nitric acid as a result of the interaction of water and nitric oxide, formed at "waterless" disintegration of NG. The fast flow of hydrolysis leads to the formation of very large quantities of nitric acid, and also glycerine dinitrate which are developed more or less abruptly by oxidizing-reduction reactions between them, accompanied by strong gas formation.

From this conclusion ensued two experimental ways of checking it, accomplished in this work.

1. Having added acid to NG together with water, we should immediately or in any case more quickly obtain that picture of flow of disintegration, which yields a neutral product on the expiration of the induction period.

2. Neutralization by any method of a forming acid must remove or at least delay the approach of that change of pressure (constancy, fast fall and accelerated growth) which is characteristic for disintegration of NG and certain other nitroesters in the presence of water.

The Influence of Acids on Disintegration of Nitroglycerine In the Presence of Water.

The influence of three acids was studied: nitric, trichloroacetic and oxalic. Nitric acid will be formed at hydrolysis and supposedly is the cause of its acceleration. However nitric acid possesses not only an acid, but also an oxidizing function, and its action could be connected also with this last one. Therefore in addition to nitric acid, we studied trichloroacetic acid, which is a strong acid, but does not have an oxidizing action, and also oxalic acid, combining the properties of acid and reducing agent.

Methodology of Experiment

Nitric acid was introduced into NG in the following way. Nitroglycerine, liberated by long evacuation in a thin layer from volatile impurities, was mixed in a determined relationship with 98.5% nitric acid. In those cases, when we investigated the influence of large quantities of nitric acid (0.15 - 1% in reference to NG), this acid NG was directly introduced into the reaction vessel. If however we studied the decomposition of NG at a smaller content of HNO_3, then into the reaction vessel we introduced prepared, as has been shown above, acid and preliminarily evacuated neutral nitroglycerine in such proportion, in order to obtain the necessary relationship between nitric acid and NG. To avoid volatilization of nitric acid, evacuation for the removal of air from the reaction vessel was done during continuous cooling of the latter by liquid nitrogen. Dosage of water was done by the usual method.

Oxalic and trichloroacetic acid were introduced into the reaction vessel in the form of aqueous solutions of determined concentration, from which the water was removed by evacuation at room temperature. The remaining operations in the preparation of the experiment remained as before.

Results of Experiments. Decomposition of nitroglycerine in the presence of small amounts of nitric acid and small quantities of water.

At decomposition of NG in the presence of a small quantity of nitric acid (initial pressure of its vapors in reaction vessel constituted 13 mm Hg which corresponds to the contents of acid approximately 0.3% by weight in reference to NG) without the introduction of water, gas formation/ occurred) fig. 1, curve 1) on the initial stage three times faster, than with pure nitroester and the time before the approach of sharp acceleration of increase of pressure was reduced approximately twice.

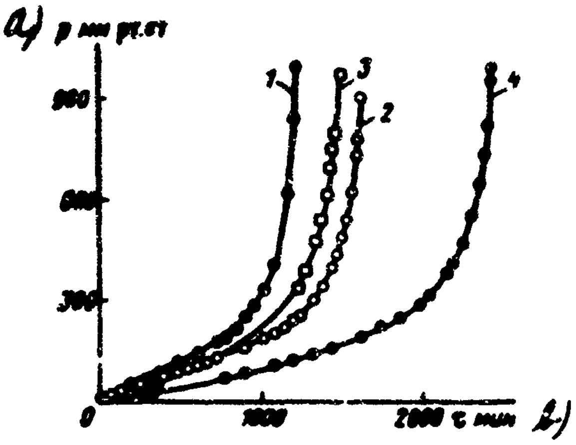


Fig. 1. Influence of small quantities of water and nitric acid on decomposition of NG at 100°. 1) NG + HNO_3, ρ_{HNO_3} = 13 mm Hg, δ = 0.0346; 2) NG+H_2O+HNO_3, $\rho_{H_2O+HNO_3}$ = 14 mm Hg, δ = 0.0281; 3) NG+H_2O ρ_{H_2O}=14 mm Hg δ = 0.0271; 4) NG pure, δ = 0.0329. a) p mm Hg; b) τ min.

The experiment, with which into NG were introduced water and acid approximately in equal quantity (curve 2), also provided faster development of the process, than it was observed in the case of pure NG. It is interesting, however that at equal equilibrium initial pressure, water (curve 3) somewhat greater accelerated decomposition of NG, than water in combination with acid.

<u>Decomposition of Nitroglycerine in the Presence of Small Amounts of Nitric Acid and Significant Quantities of Water.</u>

Experiments with ~ 0.02% nitric acid (in reference to NG) (fig. 2) and with different equilibrium initial pressures of water and acid vapors showed that the presence of such a quantity of HNO_3 does not change the general picture of disintegration: gas formation qualitatively and even quantitatively is near to that, which yields one water: the magnitude of the induction period and time before sharp acceleration of gas formation are approximately identical. Thus,

at small contents of nitric acid relatively weakly affects those peculiarities of the process of disintegration of NG, which are conditioned by the presence of water.

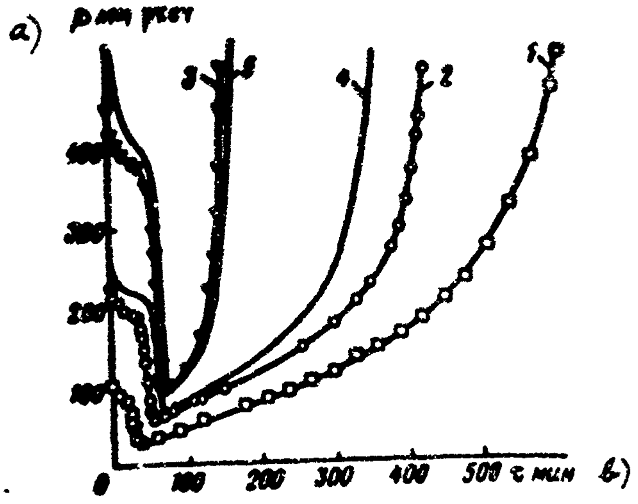
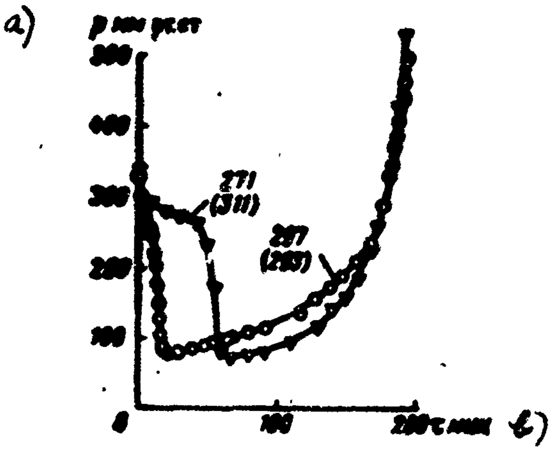


Fig. 2. Influence of small quantities of nitric acid on decomposition of NG in the presence of significant quantities of water at 100°. 1) NG $+H_2O+0.023\%$ by weight, HNO_3, $p_{H_2O+HNO_3} = 92$ mm Hg, $\delta = 0.0363$; 2) $NG+H_2O+0.017\%$ by weight HNO_3, $p_{H_2O+HNO_3} = 196$ mm Hg, $\delta - 0.0287$; 3) $NG+H_2O+0.019\%$ by weight HNO_3, $p_{H_2O+HNO_3} = 385$ mm Hg, $\delta = 0.03170$; 4) $NG+H_2O$, $p_{H_2O} = 220$ mm Hg, $\delta = 0.0290$; 5) $NG+H_2O$, $p_{H_2O} = 408$ mm Hg, $\delta = 0.0305$. a) p mm Hg; b) τ min.

Decomposition of Nitroglycerine in the Presence of Large Quantities (0.13 - 1.5% by Weight) of Nitric Acid and Significant Quantities of Water.

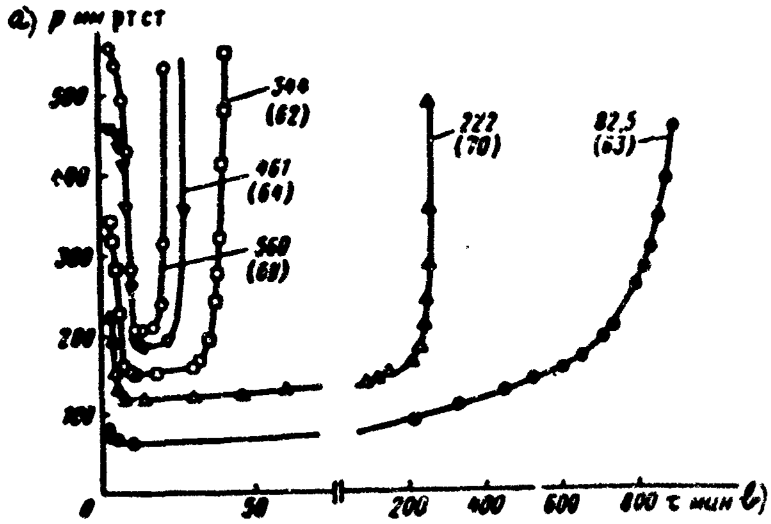
Increase of contents of nitric acid to 0.13% by weight significantly reduces the time before the beginning of fall of pressure as compared to the experiment in the presence of water, but without acid: the time, corresponding to **Pmin,** is reduced from 65 to 23 minutes. In the ulterior development of acceleration of gas formation this **quantity** of acid however almost is not reflected (fig. 3). Only a large increase of its contents (~ 1.5% by weight) greatly **reduces the time** up to the beginning of fall of pressure at decomposition of wet NG, but **also** sharply increases acceleration of gas formation.



a) p mm Hg; b) τ min.

Fig. 3. Influence of 0.13% by weight nitric acid on decomposition of NG in the presence of water at 100°. Numbers by curves - equilibrium pressure of water and acid vapors and $\delta \cdot 10^4$ (in parentheses).

In this case we can no longer speak of the induction period as a period of constancy of pressure. Having reached a maximum as the result of warm-up, pressure immediately starts to fall, after which at first is comparatively slow, but then quickly increases.



a) p mm Hg; b) τ min.

Fig. 4. Influence of 1.5% by weight nitric acid on decomposition of NG in the presence of water at 100°. Numbers by curves - equilibrium pressure of water and acid vapors and $\delta \cdot 10^4$ (in parentheses).

With this, the more water was added, the later the minimum of pressure occurred, but the more rapidly started sharp acceleration of gas formation (fig. 4).

Decomposition of Nitroglycerine in the Presence of Trichloroacetic Acid and Water.

The experiments showed that addition of trichloroacetic acid in a quantity of ~ 0.5% by weight in reference to NG greatly reduced the induction period

(τ_{min} = 48 instead of 70 minutes in the experiment with neutral NG; fig. 5, curves 1 and 2).

The presence of 2.66% by weight trichloroacetic acid completely destroys the induction period - pressure quickly falls and after 19 minutes (curve 3 passes through its minimum.

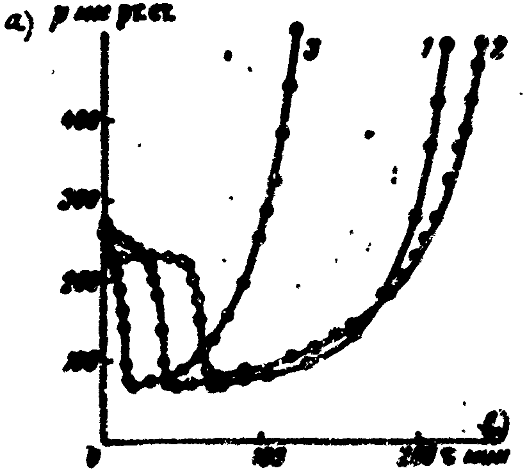


Fig. 5. Influence of trichloroacetic acid on decomposition of NG, in the presence of water at 100°. 1) NG neutral, $p_{H_2O} = 230$ mm Hg, $\delta = 0.0339$; 2) NG+0.48% by weight. TCA acid, $p_{H_2O} = 253$ mm Hg, $\delta = 0.0299$; 3) NG+2.66% by weight. TCA acid, p_{H_2O} - 230 mm Hg, $\delta = 0.0319$. a) p mm Hg; b) τmin.

This shows that the character of decomposition, observed on the initial stage of disintegration of moist NG, is conditioned by acid, and not oxidizing properties of intermediate products, formed at interaction of NG with water.

Decomposition of Nitroglycerine in the Presence of Oxalic Acid and Water.

The contents in NG of comparatively small quantities (0.08 - 0.17% by weight) of oxalic acid (fig. 6) leads to some increase of the induction period (at 0.17% from 60 to 90 minutes). In addition, in distinction from disintegration in the absence of this acid the pressure during the induction period does not remain constant, but increases, and with this all the more, acid added. Minimum pressure (after its fall) is increased, and the relative magnitude of the fall of pressure correspondingly decreases. Subsequent acceleration of gas formation is developed somewhat faster.

Lengthening of the induction period, apparently is connected with the reduction of nitrogen peroxide or nitric acid, preventing the increase of acidity of NG; the reduction taking place with the formation of gases is shown by a certain increase of pressure in the induction period; the acidity created by 0.2% by weight oxalic acid, turns out to be too small to replace nitric acid. The faster approach of acceleration of disintegration supposedly also should be connected with the reduction action of oxalic acid; oxides of nitrogen in combination with water oxidize greater, than pure nitric acid.

At an increase of the quantity of oxalic acid to 0.71 – 0.77% by weight, (fig. 7). The increase of pressure in the induction period becomes even more expressed and corresponds to the formation of 2.7 - 3.0 moles of gas per mole of oxalic acid; fall of pressure approaches a little more earlier, but occurs much less abruptly and less in magnitude.

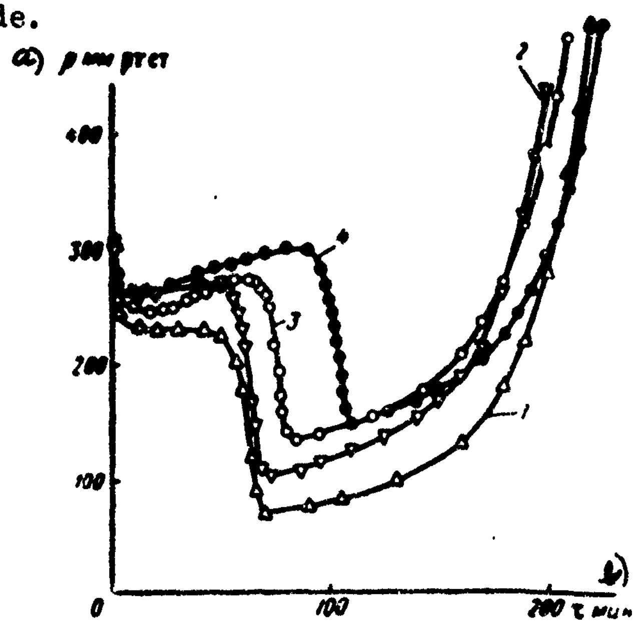


Fig. 6. Influence of small quantities of oxalic acid on decomposition of NG in the presence of water at 100°. 1) NG neutral, $\rho_{H_2O} \doteq 230$ mm Hg, $\delta = 0.0339$; 2) NG+0.078% by weight $H_2C_2O_4$, $\rho_{H_2O} = 256$ mm Hg, $\delta = 0.0326$; 3) NG+0.16% by weight $H_2C_2O_4$, $\rho_{H_2O} = 246$ mm Hg, $\delta = 0.0313$; 4) NG+0.17% by weight $H_2C_2O_4$, $\rho_{H_2O} = 262$ mm Hg, $\delta = 0.0318$. a) p mm Hg; b) τ min.

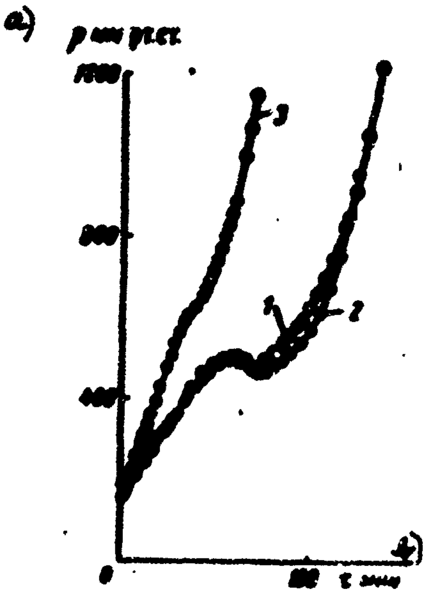


Fig. 7. Influence of significant quantities of oxalic acid on decomposition of NG in the presence of water at 100°. 1) NG+0.71% by weight $H_2C_2O_4$, $P_{H_2O} = 175$ mm Hg, $\delta = 0.0404$; 2) NG+0.77% by weight, $H_2C_2O_4$, $P_{H_2O} = 191$ mm Hg, $\delta = 0.0326$; 3) NG+1.62% by weight $H_2C_2O_4$, $P_{H_2O} = 160$ mm Hg, $\delta = 0.0358$. a) p mm Hg; b) τ min.

At even larger contents of oxalic acid (1.6%) there is still no fall of pressure and only a certain brief delay of its increase is observed. Obviously, with this concentration is developed already the accelerating action of oxalic acid on hydrolysis, and its reduction action, increasing the concentration of nitrogen oxides, accelerates and strengthens oxidation and the increase of pressure determined by them. As a result both stages - hydrolysis and oxidizing reduction reactions - are not divided clearly in time, as this is observed only in the presence of water, and are placed by one another and even converge (fig. 7, curve 3).

Influence of Soda and Chalk On Disintegration of Nitroglycerine in the Presence of Water.

Neutralization of acid products of disintegration of NG by means of soda was produced by two methods: introduction of slight quantities of it in a reaction vessel[1] or soldering an ampoule to the latter, containing a significant quantity of Na_2CO_3. The advantage of the first method included the fact that due to the close contact of NG with soda, fast neutralization of the acids formed occurred.

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[1] Soda was introduced in a reaction vessel in the form of an aqueous solution of determined concentration, from which water was removed by evacuation at room temperature.

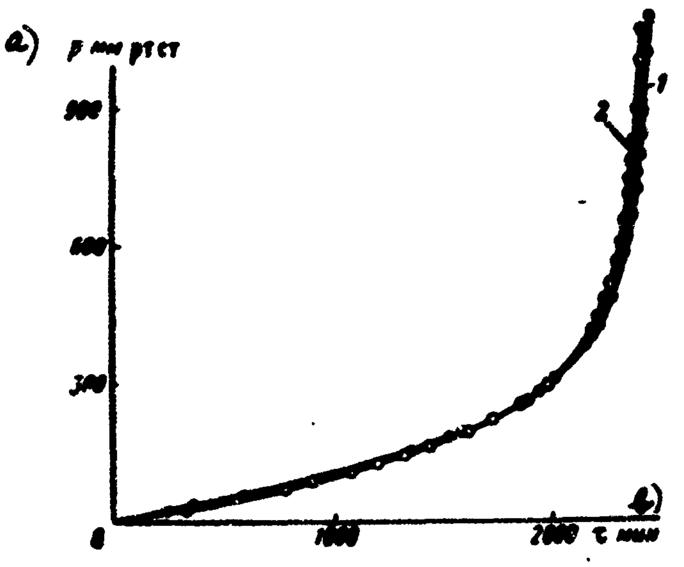

Fig. 8. Influence of slight quantities of soda on decomposition of Anhydrous NG at 100°. 1) NG+0.068% by weight Na_2CO_3, δ = 0.0318; 2) NG neutral, δ = 0.0329. a) p mm Hg; b) τ min.

To the shortcomings of this method one should relate the possibility of saponifying action of soda on nitroglycerine. Only volatile acids can be neutralized by the second method and, in addition, their speed of entrance into the ampoule with soda is limited by diffusion through a layer of water vapors in the connecting tube.

Before conducting decomposition of NG at the joint presence of water and soda an experiment was set up with anhydrous NG with a small quantity of soda introduced into it. Fig. 8 shows that soda, at least in small quantities, does not have noticeable influence on disintegration of anhydrous NG.

Otherwise there is the matter in the case of wet NG. The presence of soda significantly increases the time to the beginning of fall of pressure. Thus, in the presence of 0.044% by weight Na_2CO_3 (fig. 9, curve 4) the duration of the induction period was approximately 120 minutes, at the time when in the case of neutral NG with such an initial pressure of water vapors the fall of pressure began after 40 min. Besides, in the presence of soda the pressure for the duration of the induction period does not remain constant, but somewhat increases (on 5-7 mm Hg). Minimum pressure is increased somewhat and its relative lowering correspondingly decreases (0.62 instead of 0.71).

Fig. 9. Influence of small quantities of soda on decomposition of NG in the presence of water at 100°. 1) NG neutral, $\rho H_2O = 293$ mm Hg, $\delta = 0.0367$; 2) NG+0.053% by weight Na_2CO_3, $\rho H_2O = 311$ mm Hg, $\delta = 0.0316$; 3) NG neutral, $\rho H_2O = 230$ mm Hg, $\delta = 0.0339$; 4) NG+ 0.044% by weight Na_2CO_3, $\rho H_2O = 236$ mm Hg, $\delta = 0.0377$. a) p mm Hg; b) τmin.

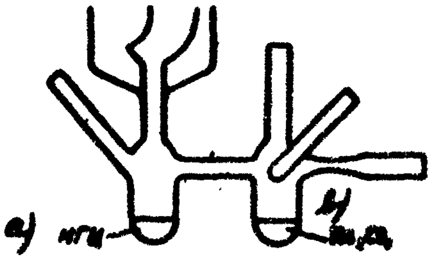

Fig. 10. Reaction vessel for decomposition of NG in the presence of large quantities of soda and chalk. a) Mg b) No_2CO_3

Apparently, the formed acid is neutralized by soda, and when the latter reacts completely, usually enters in the presence of water a fall of pressure and its subsequent accelerated increase. The lesser solubility of CO_2 in nitroglycerine, formed at neutralization of soda, as compared with nitric acid should be explained by a certain increase of pressure in the induction period and increase of ρ_{min}. Further increase occurs somewhat slower, than in the absence of soda.

An even longer retardation of disintegration of NG in the presence of water can be obtained, if one were to ensure neutralization of acid volatile products of disintegration. For that, a comparatively large quantity of soda or chalk (5-9 times more than NG) was introduced into a lateral ampoule, soldered to the reaction vessel (fig. 10). Pressure of water vapors in the beginning of the experiment constituted 135 mm Hg. In this case gas formation began with significant speed[1] (fig. 11, curve 2), which later began to decrease and after 125 hours was lowered to its own constant value, near in magnitude to the initial speed of gas formation of anhydrous NG. The increase of pressure with such constant speed in the future was continued for the duration of 30 days[2]. An anhydrous form of the curve $p = f(\tau)$ was observed at decomposition of anhydrous NG in the presence of a large quantity of soda (curve 3), but the initial speed of gas formation in this case was somewhat more higher. On a section of constancy its values in both cases were near in magnitude (cf. curves 2 and 3 fig. 11).

Both at disintegration of anhydrous NG, and also in the presence of water was not observed any acceleration of gas formation in spite of the fact that pressure toward the end of the experiment exceeded two atmospheres.

In both cases the gas phase during the entire experiment remained colorless. Soda in the movement of the decomposition took on a brown color, probably due to polymerization and resinification on it of intermediate products of disintegration; the walls of the reaction vessel were coated with a white deposit.

Acceleration of gas formation was absent however, in those experiments in which soda was replaced by chalk (fig. 11, curve 4). It is characteristic that in this case a section was not observed with great initial speed of gas formation: decomposition for the duration 20 days went with constant speed, approximat

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[1] Supposed as a result of interaction of NG vapors with soda on the surface of its particles.

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[2] In the course of the experiments several times breaks were taken (every 30 hours), marked on the graph. After interruption, the pressure always was several millimeters less than before it.

ly equal to the initial speed of disintegration of anhydrous neutral NG.

a) p mm Hg
b) τ min.
c) interruption

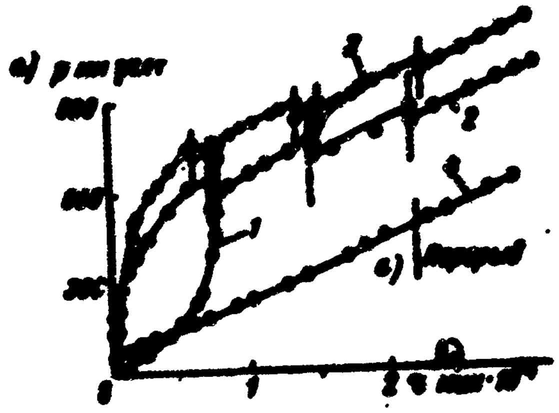


Fig. 11. Decomposition of dry and wet NG in the presence of large quantities of soda and chalk 100°. 1) NG without water and soda, $\delta = 0.0067$; 2) $NG+H_2O+Na_2CO_3$, $p_{H_2O} = 135$ mm Hg, $\delta = 0.0063$; 3) NG $+Na_2CO_3$, $\delta = 0.0074$; 4) $NG+CaCO_3$, $p_{H_2O} = 62$ mm Hg, $\delta = 0.0075$.

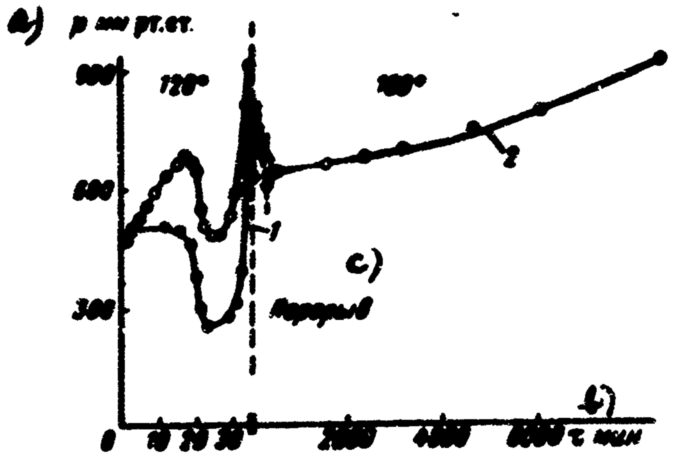
Anhydrous NG without soda ($\delta = 0.0067$) (fig. 11, curve 1) in these conditions starts to decompose rapidly already after ~ 130 hours, and in the presence of water considerably earlier.

In the experiments conducted at 100° acceleration of gas formation did not occur, only under the condition that decomposition went with not a very large speed and products of disintegration succeeded to be diffused through a layer of liquid and gas to soda. Conversely, there is a fall of pressure and its subsequent accelerated increase which was observed at decomposition of NG in the presence of water at 120° and $\delta = 0.0051$ (fig. 12, curve 2). If after interruption at the stage of sharp acceleration of increase of pressure temperature of the experiment is lowered to 100°, then strong acceleration of gas formation does not occur for the duration of the subsequent 130 hours of heating (fig. 12, curve 2 after interruption).

Discussion of Results.

Results of experiments confirm and make certain those assumptions for checking of which they were set up.

Introduction of nitric acid into wet NG can significantly reduce and even eliminate the induction period. In the case of anhydrous nitroglycerine, the



a) p mm Hg
b) τ min.
c) interruption

Fig. 12. Decomposition of NG in the presence of large quantities of soda at 120° and 100°. 1) NG without soda, $\rho\, H_2O$ = 505 mm Hg, δ = 0.0066: 2) NG+Na_2CO_3, ρH_2O = 466 mm Hg, δ = 0.0051.

influence of nitric acid is expressed much more weaker, and even a significant content of it (0.3% by weight in reference to NG) only twice reduces the time to the onset of sharp acceleration of disintegration of nitro ester.

One should note that small quantities of nitric acid, even in the presence of water, hardly accelerate disintegration. This refers both to small, and also to significant contents of water.

If the quantity of added nitric acid exceeds 0.1% by weight NG, significant reduction of induction period is observed. On subsequent acceleration of gas formation this is not reflected, since to the moment of its onset as a result of hydrolysis will be formed much more acid and an additional increase of its quantity to 0.1% is relatively very little and cannot noticeably affect development of the process of decomposition of nitro ester.

Addition of 1.5% by weight nitric acid to wet NG not only eliminates the induction period, but also leads to significantly faster development of subsequent gas formation.

Unfortunately, accurate quantitative estimate of the influence of actual concentration of nitric acid and water in NG in reference to these experiments is hampered by several causes. First, it is unknown, how at the joint presence in the reaction vessel of water and nitric acid with NG they are distributed between the gas and liquid phases; this distribution can be all the more so essential that the experiments were conducted at relatively small δ and high (100°) temperature, when the relative contents of acid and water vapors in the gas phase can be significant. Secondly, the method of water dosage is used, based on measurement of volume its vapors at relatively low room temperature, could be connected with noticeable inaccuracy due to adsorption of them on the walls of the measuring ball. Third, solubility of water in NG, containing those or other additionally introduced substances (for example, trichloroacetic acid, soda), can be distinguished from its solubility in pure nitro ester.

More reliable are the quantities of nitric acid introduced into NG and equilibrium total pressure of water and acid vapors, measured at the temperature of the experiment. In exactly the same way the basic fixed regularities of decomposition of wet NG in the presence of HNO_3 do not evoke doubts: reduction of duration of induction period, significant amount necessary for that concentration of HNO_3 and smaller sensitivity of the period of acceleration to it.

Experiments with trichloroacetic acid confirm that the primary factor of the influence of acids, including nitric, on the decomposition of wet NG is their accelerating action on hydrolysis, and not the oxidizing function and that this last action becomes strong only at significant contents of nitric acid in NG.

This is confirmed also by experiments with oxalic acid. Its small contents in NG (up to ~0.2% by weight) extends the induction period, since acceleration of hydrolysis with these quantities of $H_2C_2O_4$ is small, but inhibition of the formation of nitric acid as a result of reduction of higher oxides of nitrogen is great. At large (0.7 - 1.6%) contents of oxalic acid, acid action predominates and relatively fast reduction of nitric acid and partial transition of it due to this in oxides of nitrogen leads to the more early development of gas-forming oxidizing-reduction reactions, which are not separated in this case from hydrolysis by a certain interval of time.

Still more convincing for confirmation of the main conclusion - about the decisive role of hydrolysis as the "release" mechanism for the development of transformation of NG are the results of experiments with soda and especially with chalk. They show, first that a necessary condition for the beginning of the fall of pressure of water vapors and subsequent acceleration of gas formation is the accumulation of acids, and secondly, that these acids are volatile. Speed of hydrolysis in the absence of acid is low. Therefore hydrolysis then starts to play its decisive role, when will be formed sufficient concentration of acid. Quantity of the latter has to correspond to the quantity of water in NG if there is little water, then a sufficiently small quantity of acid, so that its concentration, and consequently, the magnitude of constant of speed of catalyzed hydrolysis is great. Since, the speed of hydrolysis is proportional to the product of the constant and the concentration of water, then the influence of acid on the constant of speed can predominate above the influence of the concentration of water, and on the whole process of hydrolysis (but not gas formation) will be developed faster, than in the presence of large quantities of water.

If there is much water, then it is required to add more acid and by this to create a condition for fast development of hydrolysis. In this case also, the subsequent acceleration of the process of disintegration of NG goes faster, since will be formed more acid as a result of "transformation" of water into it, and besides, acid is added to it, introduced into nitro ester in the beginning of the experiment.

Thus, the most dangerous under the conditions of long stay at increased (100°) temperatures[1] is slightly moistened NG, if it is insufficiently thoroughly

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[1] At lower (60°) temperatures, as show the experiments of Gorbunov and Svetlov, the stage of acceleration of disintegration of NG is attained the faster, the more water dissolved in the nitro esters.

washed from acid. Greatly moistened and especially containing liquid-drop water product is less dangerous. Less dangerous would be also an absolutely anhydrous product, but in such a state nitroglycerine is practically not real, inasmuch as even very small concentrations of water in NG, corresponding of its partial pressure in the surrounding atmosphere of 8 - 15 mm Hg are effective. Presence in nitro esters of impurities, not possessing considerably expressed alkalinity, but able to neutralize acid (for example, chalk), prevent the development of hydrolysis and subsequent acceleration of decomposition of nitroglycerine.

CONCLUSIONS

1. Nitric acid in small concentrations slightly accelerates decomposition of nitroglycerine in the presence of water. Increase of concentration of acid to ten fractions of a percent leads to fast development of hydrolysis of NG; at even larger increase of quantity of acid the development after hydrolysis of oxidizing-reduction reactions is also accelerated.

2. Hydrolysis of NG is accelerated also by trichloroacetic and oxalic acids. In the last case however, at small concentrations of acid, hydrolysis lags due to the reduction action of $H_2C_2O_4$ on the products of "anhydrous" disintegration.

3. Substances, neutralizing acids (soda, chalk), prevent (at disintegration of NG in the presence of water) fast development of hydrolysis and subsequent acceleration of gas formation as a result of the oxidizing-reduction reactions between the products of hydrolysis.

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Pages [illegible]-189 Article No. 11

B. S. Svetlov

11. On the Thermal Decomposition of Nitroglycerine in the Liquid-Phase.

Study of the thermal decomposition of polynitro esters presents great theoretical and practical interest. However the explanation of the mechanism of their disintegration is strongly hampered by its complexity. As is shown by investigation [9], the decomposition even of alkylmononitrates in the gaseous phase is a complex of parallel and sequential reactions. Decomposition of polynitrates, studied in less detail, especially in the liquid phase, under conditions leading to sharp self-acceleration, represents an undoubtedly a still more complicated process [4], [5].

In this work is described passed in interval of temperatures 80-140° investigation of thermal decomposition in liquid phase of one of the most important nitro esters-nitroglycerine (NG) and, in particular, its self-accelerated disintegration.

Study of the decomposition of NG was conducted by the manometric method with application of a glass manometer of type of Bourdon [5]. Ratio of the volume of nitro ester to that of the reaction vessel, designated hereafter as [illegible], constituted 10^{-3} to 10^{-1}.

Decomposition of nitroglycerine represents, at least, a two-phase process [4]. This can be seen especially clearly in examining the dependence of the speed of gas formation from pressure in logarithmic coordinates (Fig. 1), where the course of disintegration is described by two straight lines, proceeding under various angles. Each of these two macroscopic stages of decomposition possesses its own characteristic features.

On first stage no sharp self-acceleration is observed even during the accumulation of significant quantities of gasiform products. Hence it was at this time conducted, despite generally-held earlier presentations, that gasiform products in these conditions do not display a catalytic action on the thermal disintegration of nitroglycerine [1].

Disintegration of nitroglycerine in first stage can be characterised by the mean magnitude of the initial speed of gas formation, calculated for the interval of pressure of products of disintegration from its beginning to 40-80 mm Hg. Such a calculation is not fully accurate, since in certain cases in the initial section of the first stage there occurs a small growth in speed, clearly developed at higher temperatures and significant degrees of filling of the reaction vessel. Gas formation with this can be accelerated in the indicated interval of reading of speed by 1.5-2 times.

The value of δ shows significant influence on the initial speed of gas formation. In all studied intervals of temperatures (140-80°C) initial speed of gas formation falls with an increase in δ.

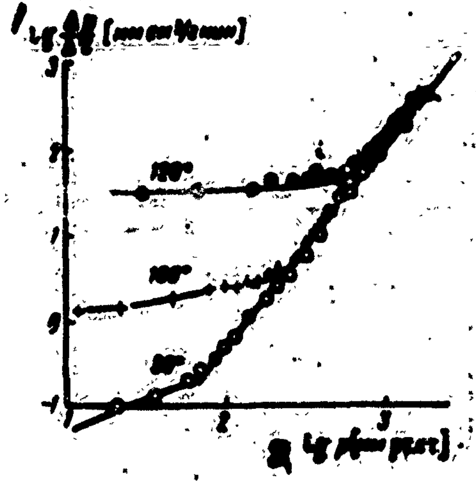

Fig. 1. Influence of pressure of gasiform products of decomposition of nitroglycerine on its disintegration at different temperatures and $\delta = 0.03$. 1--Log $\Delta p/\Delta \tau$ [mm cm^3/g·min]; 2--Log p [mm Hg].

Pre-exponential multiplier B in Arrenius' equation corresponds to $10^{18.4}$ and $10^{15.4}$ sec^{-1} for small and large δ, respectively.

The first of the values obtained for E and B are near to those calculated according to the data of Robertson. From the speed of splitting-off of nitrogen during the decomposition of nitroglycerine in a stream of carbon dioxide gas [10]. Calculation according to Robertson gives E = 43.7 kcal/mol and B = $10^{18.64}$ sec^{-1}. Magnitude of E, obtained for large δ is near to the energy of breakaway of NO_2 during the disintegration of alkylmononitrates: 395.5 kcal/mol for methylnitrate [6] and 41,2 kcal/mol for ethylnitrate [9].

In connection with this one should note that the decomposition of nitroglycerine is characterized in the first stage by presence of nitrogen peroxide in the gasiform products of disintegration which can be judged by the change of color of the gaseous phase (browning), noticeable to the eye, and also by special colorimetric experiments, the results of which showed that the fraction of NO_2 in the gases reaches 40-60 % [8].

The second stage of decomposition of nitroglycerine, the stage of sharp acceleration of gas formation, sets in only under the condition, that the pressure of the formed gases attains a definite critical value, which in a significant interval of δ (10^{-3}--10^{-1}) is a magnitude approximately constant for a given temperature and, consequently, does not depend on the degree of decomposition.

Flow of decomposition abruptly changes during transition to the second stage. If in the first stage (in the section of the induction period) the speed of gas formation increased only by 2--3 times and was proportional to pressure in a degree significantly less than unity, then in the second stage it becomes proportional approximately to the square of the pressure of the gasiform products of decomposition (Fig. 1) and can exceed the initial speed by a hundred times. An analogous picture of disintegration was obtained for nitroglycol, and also, according to the

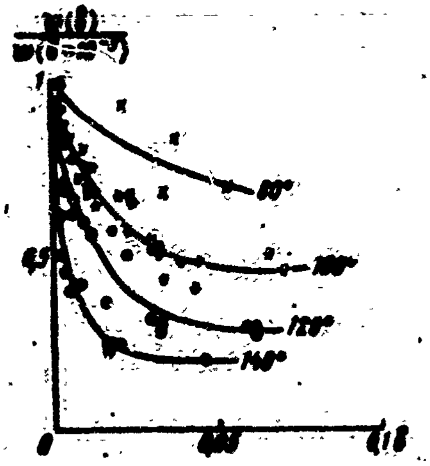

Fig. 2. Influence of degree of filling of reaction vessel on the initial speed of gas formation during the disintegration of nitroglycerine. $\frac{w\,\delta}{w(\delta=10^{-3})}$ ratio of initial speed at given δ to its value at $\delta = 10^{-3}$.

In fig. 2 is represented the dependence of initial speed of gas formation on the magnitude of δ. For consideration of this dependence at different temperatures there are given not absolute values of speed, but the ratio of initial speeds at corresponding values of δ to initial speed at $\delta = 10^{-3}$. As can be seen from the graph, the influence of δ on initial speed of gas formation is developed more abruptly with growth in temperature. In the region of small δ initial speed stronger depends more strongly on the degree of filling of the vessel than in region of high δ and at δ $3 \cdot 10^{-2}$ it practically no longer changes.

It is necessary to note in connection with this that the lowering of initial speed with growth of δ is a general regularity for the disintegration of many studied liquid nitro esters: for melting pentaeryithritetetranitrate according to the data of B. I. Kaydymov, and also for nitroglycol, diglycoldinitrate and dinitrates of glycerine by our data. At the same time B. S. Samsonov [2], [3] established that the degree of filling of the vessel does not affect the initial speed of gas formation during the disintegration of nitrocellulose.

The explanation of this phenomenon is hampered by the absence of data on the details of the mechanism of nitro ester decomposition. However, it is possible to consider that the causes stimulating the influence of δ on the initial speed of gas formation lie not so much in the solubility of gases or in the high speed of disintegration of nitro esters in the gaseous phase [5], as in the flow of secondary processes of oxidation of organic substances by nitrogen peroxide, the speed of which is connected with the degree of disintegration, possibly in combination with the reversibility of the reaction of primary breakaway of NO_2 from the molecule of the nitro ester.

In view of the significant and quantitatively different influence of δ on the magnitude of the initial speed at various temperatures, evaluation of the temperature dependence of the speed of gas formation was done somewhat formally; it was determined separately for $\delta = 10^{-3}$, i. e., for that degree of filling of the reaction vessel, in whose region it strongly affects initial speed, and for $\delta = 10^{-2}$, at which the initial speed of gas formation becomes practically constant.

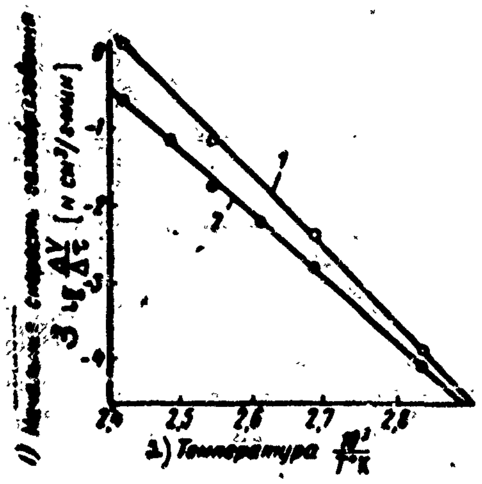

Fig. 3. Influence of temperature on initial speed of gas formation during disintegration of nitroglycerine. 1- $\delta = (10 \text{ to } 30) \cdot 10^{-4}$; 2- $\delta = (300 \text{ to } 450) \cdot 10^{-4}$. 1) Initial speed of gas formation; 2) Temperature, $10^3/T°K$; 3) Log $(\Delta V/\Delta \tau)$ [n $cm^3/g \cdot min$]

In both cases the dependence of speed of gas formation on temperature is subordinated to the equation of Arrenius. Activation energy E, calculated by the tangent/of/ angle of inclination of the line in coordinates log $(\Delta p/\Delta \tau)$ init.-(1/T), for small δ constitutes 43.6 kcal/mol and for large δ, 39.3 kcal/mol (Fig. 3).

data of B. I. Kaydymov, for solutions of pentaerythrite tetranitrate in tetryl at 120°.

The magnitude of the critical pressure depends on temperature, increasing with an increase in the latter. Thus at 80° ($\delta = 6\text{-}60 \cdot 10^{-3}$) it constitutes 60-80 mm Hg; at 100° ($\delta = 1.5\text{-}60 \cdot 10^{-3}$)180-210 mm Hg and at 120° ($\delta = 3\text{-}60 \cdot 10^{-3}$) 400-500 mm Hg. Experiments at 140° with $\delta = 15 \cdot 10^{-3}$ and $29 \cdot 10^{-3}$ gave 1000 and 800 mm Hg, respectively; at a smaller degree of filling of the reaction vessel, the decomposition of nitroglycerine at this temperature did not pass into the second stage, in spite of the fact that the pressure of the gasiform products attained 3500mm Hg during disintegration.

The presence of critical pressure, not depending directly on the degree of disintegration, and also the original character of the decomposition of nitroglycerine in the second stages are connected, apparently, with reactions, in which there is participation of gasiform products dissolved in the condensed phase.

It is possible to allow that the decomposition of nitroglycerine in the liquid phase proceeds in two ways. To the first way correspond reactions which are not accelerated by the gasiform products of disintegration. The speed of this process does not grow with pressure. The alternate way is the disintegration of nitroglycerine during its interaction with products of decomposition; the speed of this process is proportional to the square of the pressure of gaseous products of disintegration. It is natural to assume that the initial speed of gas formation characterizes flow of disintegration by the first way, and that the acceleration observed in experiments is the result of the development of disintegration reactions of nitroglycerine by the alternate path. Hence for the initial stage, when the decrease in the concentration of parent substances can be neglected, the total speed of gas formation is $\frac{dp}{d\tau} = w + kp^2$, where w-speed of the process not accelerated by pressure, i. e., the initial speed of gas formation, p-pressure of gasiform products, and k-proportionality factor. If shown considerations are correct then curves of $(\frac{dp}{d\tau} - w) = f(p)$ in logarithmic coordinates must be expressed by straight lines with tangents of the angle of inclination of nearly two. Processing of results of experiments shown in Fig. 1, indeed shows that in these coordinates a straight line is obtained if for w we take a value, close to the initial speed of gas formation (Fig. 4, line 1). For graphic comparison, the curve of dependence of speed of total gas generation on pressure for experiments at 100° is given (curve 2).

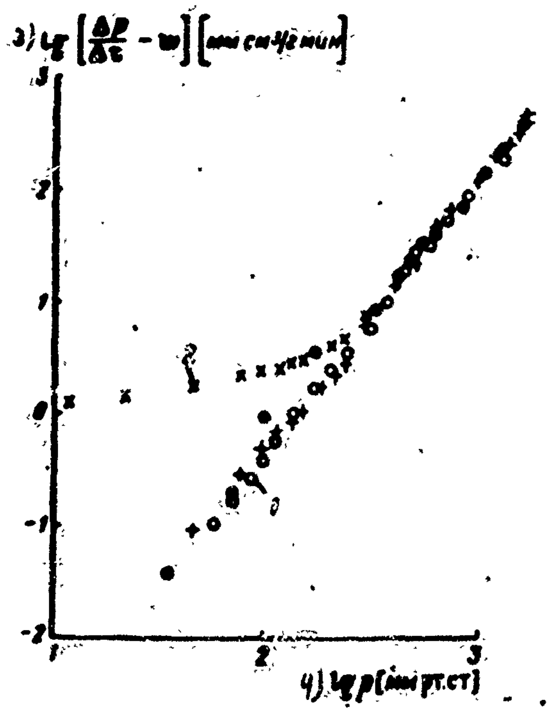

Fig. 4. Influence of pressure of gasiform products of decomposition of nitroglycerine on the increase of speed of gas formation above its initial value at different temperatures. 1-at 80, 100 and 120°; 2-influence of pressure on general speed of gas formation at 100°; 3-log $[\frac{\Delta p}{\Delta \tau} - w]$ [mm cm³/g·min]; 4-log p [mm Hg].

Proceeding from the presented, [material], it follows to assume that the beginning of the second stage of disintegration is conditional and corresponds to that moment, when the concentration in the liquid phase of products of disintegration which accelerate the reaction becomes significant and the speed of their interaction with the parent substance starts to predominate over the speed of reactions whose course is not accelerated by the products of disintegration.

In favor of the assumption of the leading role of gaseous products of disintegration during the self-accelerated decomposition of nitroglycerine, there are experiments with pure nitroglycerine in the presence of gasiform products obtained in other experiments during the decomposition of this nitro ester at the stage of sharp acceleration. With addition of these products the speed from the very beginning of the experiment exceeds by tens and hundreds of times the initial speed of gas formation during disintegration of pure nitroglycerine. With this, the greater the addition of products, the higher is the speed of disintegration.

The process of the decomposition of nitroglycerine in the second stage appears, evidently, principally as the hydrolysis of the nitro ester with the formation of acid in conjunction with oxidation reactions, generating water.

The established influence of temperature on magnitude of critical pressure can be conditioned on the one hand by a change of solubility of gases with temperature and on other by the fact that the speed of the reaction which is not accelerated by products of disintegration (primary reaction) grows faster with temperature than that of reactions which depend on pressure. As a result of this, in order for the speed of reactions, which depend on pressure to exceed noticeably the speed of the reaction which does not depend on it, at higher temperatures a large concentration of gasiform products of disintegration in liquid phase is necessary.

The second stage of decomposition of nitroglycerine is characterized by an extremely weak influence of temperature on the speed of gas formation. As can be seen from the graph (Fig. 1) at pressures above the critical, i. e., in the section of sharp acceleration, the points of dependence $\log \frac{dp}{d\tau} = f(\log p)$ at 80, 100 and 120° lie on practically one line, i. e. , the speed of gas formation depends only on the pressure of the products of decomposition and not on temperature. The dependence characterizing the course of reactions of disintegration of nitroglycerine by the second path at these same temperatures (Fig. 4) also constitutes a single line. The absence of an influence of temperature on the speed of gas formation during the disintegration of nitroglycerine, conditioned by the interaction of products of ester decomposition, may be connected with the fact that with an increase in temperature, the increase in the speed of the reaction is compensated by a decrease in the concentration of reacting substances due to the lowering of solubility of gasiform products in nitroglycerine. Therefore, in the given case the temperature dependence of speed of process should be estimated with the influence of temperature on the solubility of products of disintegration in condensed phase taken into account. If one were to begin from the assumption of compensation of increase of disintegration rate with temperature by a decrease in the solubility of gases, then it is possible to consider that the activation energy of the reaction of decomposition of nitroglycerine with participation of gasiform products will be near to their heat of dissolution in this nitro ester. Thus, since the heat of dissolution of gases in liquids is as a rule, small as compared with the activation energy of the primary reaction of disintegration of nitroglycerine (40 kcal/mol), the activation energy of leading reactions on second stage is also small.

This circumstance, important for evaluating the stability of nitro esters, should be considered in studying the behavior of these substances during storage and processing. In real conditions, when the removal of products of disintegration from the mass of the substance is hampered (large volume and low temperature), the decomposition of a nitro ester is determined basically by its interaction with these products; this interaction possesses a sharply self-accelerated character and small temperature coefficient of speed. Therefore a characteristic of the disintegration of nitroglycerine, determining its stability during storage and processing, is the magnitude and temperature dependence of the induction period, during which the conditions of development of subsequent reactions are formed.

Conclusions

1. Thermal disintegration of nitroglycerine in liquid phase during 80-140° in presence of products of decomposition was investigated.

2. The presence during the disintegration of nitroglycerine of two macroscopic stages, whose course depends only on the contents of products of disintegration, but not on its depth, was established.

3. On first stage of decomposition gasiform products of disintegration show practically no accelerating effect on the speed of gas formation. The initial speed of the latter depends on the degree of filling of the reaction vessel and is characterized by the normal temperature coefficient of this speed for nitro esters.

4. In the second stage of decomposition the speed of gas formation depends on the pressure of gasiform products of disintegration approximately to the second degree and can exceed the initial speed by at least a hundred times.

5. The results obtained are considered in the light of the assumption of a simultaneous flow of two processes of decomposition of nitroglycerine. The first of them represents spontaneous decomposition, not accelerated by gasiform products of disintegration. During the second process there occurs interaction of nitroglycerine with products of its disintegration, as was assumed by S. Z. Roginskiy [7], with the speed depending on contents of these products.

Author expresses great gratitude to K. K. Andreyev for his constant interest in the work.

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Tape No. MT-63-254 Chapter 2 Article 12

Pages 190—196

V. V. Gorvunov and B. S. Svetlov

12. Concerning the Influence of Temperature On Decomposition of Nitroglycerine

Thermal disintegration of nitroglycerine and other nitro ester in liquid phase is investigated basically at a comparatively high temperature, but also relatively small degree of filling of ampule in the case of application of manometric method [1], [2], [3] and [4]. The results obtained with this, interesting from the point of view of explaining the mechanism of decomposition, cannot be, however, directly used for description of behavior of nitro esters under the conditions most interesting from the point of view of practice, i. e. during low temperature and maximum concentration of products of disintegration in substance.

In order to reproduce the indicated conditions of disintegration, we applied the method described earlier [1], modifying it for maximum filling of preliminarily evacuated ampule and glass monometer united with it with liquid nitro ester.

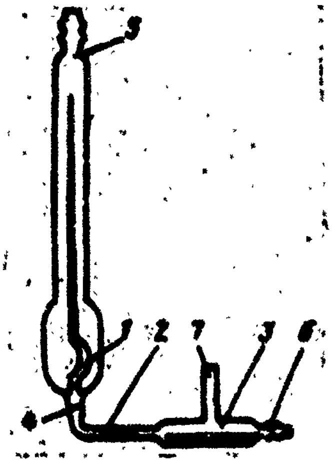

Fig. 1. Diagram of instrument for study of thermal decomposition of liquid nitro ester during maximum filling of ampule.

1) manometer with pointer, 2) intake 3) vessel for evacuation of nitro ester during preparation of experiment, 4) reaction vessel, 5-6) drains for connecting instrument with vacuum installation, 7) branch for entrance of niteo ester.

For preparation and effectuation of such experiments we used the instrument, depicted in fig. 1. Glass manometer 1 with the thin intake 2 united with vessel 3, are intended for preliminary evacuation of nitro ester in a thin layer. The experiment was prepared in the following manner. At first we measured the internal volume of reaction vessel 4 and glass manometer to the place of subsequent resoldering of intake 2, by means of weighing the instrument with water. After determining the volume the instrument was joined to the vacuum installation with the help of connecting rubber tubes, put on crimped branches 5 and 6 of the glass manometer and vessel. Through branch 7 in vessel 3 we placed the exact weighed amount of nitro ester (nearly 1 g), after which this branch was soldered. Nitro ester, in a thin layer, was pumped not less than 6 hours at a pressure of 10^{-4}-- 10^{-5} mm of mercury to full removal of volatile impurities, which was judged by the absence of pressure increase in the instrument after disconnecting the pumps. Then nitro ester was transfused into the internal cavity of the glass manometer. Surplus of nitroester, under light heating by a stream of water vapor, was driven from intake back into vessel 3. The intake, after being completely purified of traces of nitroglycerine, was quickly resoldered and the instrument disconnected from the vacuum installation. The quantity of nitro ester in the instrument was judged by the difference between the initial weighed amount and the weighed amount, remaining after resoldering of intake 2 in vessel 3. The prepared instrument was connected by drain 5 with the mercury manometer, placed in liquid thermostat and the increase of pressure of gasiform products of disintegration in time was measured. Before measurements it was necessary to mix contents of instrument by repeatedly driving the gas bubble from manometer 1 to the lower part of reaction vessel and back again; since otherwise, pressure, especially in the beginning of the experiment, either barely grows or grows nonuniformly, which is due, apparently, to the great thickness of the layer of nitro ester in which diffusion of gases proceeds slowly.

Decomposition of nitroglycerine at a degree of filling (Δ), close to one, was investigated at 40-100°.

Disintegration in these conditions is characterized by the presence of two macroscopic stages, similar to that, which was observed at higher temperature and significantly smaller degrees of filling of reaction vessel.

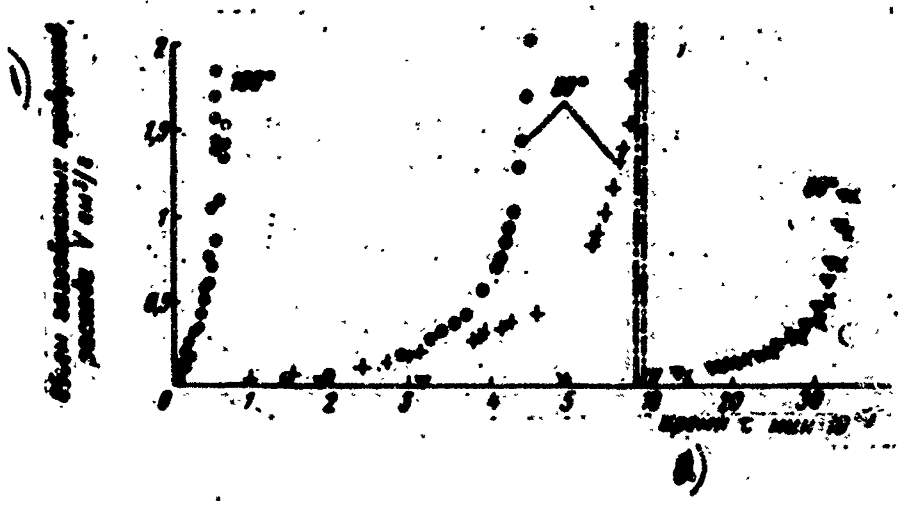

Fig. 2. Change of gas formation in time during decomposition of nitroglycerine at $\Delta \approx 1$ and different temperatures.

1) Volume of gasiform products of disintegration V cm^3/g; 2) Time τ min. 10^{-3}.

Fig. 2 presents curves of change of volume of gasiform products of disintegration in time for parallel experiments at $\Delta \approx 1$ and temperature 60, 80 and 100°[1].

As can be seen from graphs presented, in the beginning of disintegration gas formation, especially during low temperature, proceeds slowly for a long time. After induction period gas formation starts abruptly growing, attaining magnitudes, exceeding its initial rate hundreds of times.

Under detailed consideration of results received it turns out that analogy with experiments at small Δ is limited in many respects only by the qualitative side.

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[1] In experiments at 40°, the duration of which reached 8 months, sharp acceleration was not attained.

Fig. 3. gives in coordinates $\lg \frac{\Delta V}{\Delta \tau} - \frac{1}{T}$ dependence of initial rate of gas formation on temperature, characterizing disintegration of nitroglycerine in the first stage. This dependence is expressed by the straight line, however, the tangent of its angle of inclination is significantly less than in experiments under increased temperature with small δ[1], correspondingly activation energy in our experiments constitutes only 29, instead of 40 kilocalorie/gram-molecule for the case of small degrees of filling of reaction vessel. In other words, the temperature coefficient of initial rate of gas formation during disintegration of nitroglycerine under the conditions of our experiments is significantly less than that, which can be obtained, extropolating, for example, the results of Robertson [5], and also our data for small δ at low temperatures. Ratio of rates at 60 and 40°, obtained by extrapolation, constitutes nearly 50-60, during the experiment it showed a magnitude of nearly 16.

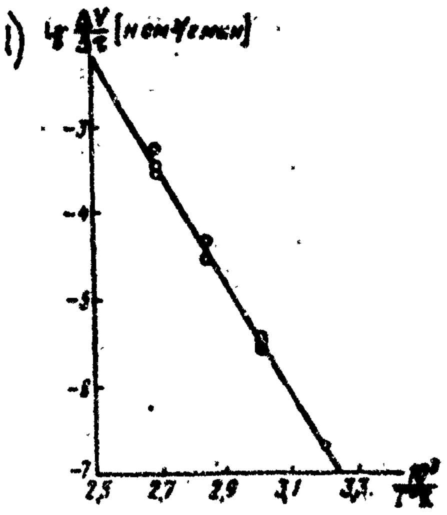

Fig. 3. Influence of temperature on initial rate of gas formation – during disintegration of nitroglycering at 40-100°. 1) log $\frac{\Delta V}{\Delta \tau}$ [n cm^3/г min]

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[1] Results of investigations of disintegration of nitroglycerine in liquid phase at small degrees of filling and the higher temperatures are presented in the preceding article of the present collection.

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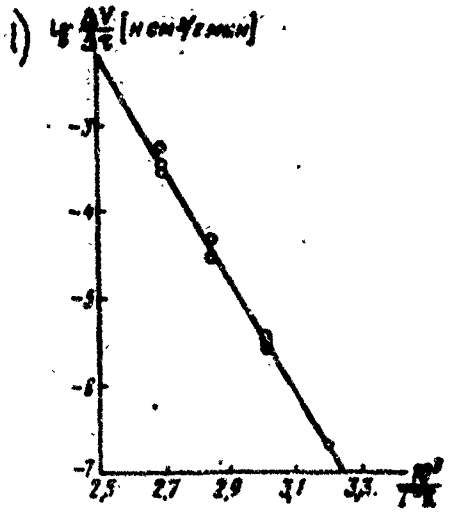

Fig. 3. Influence of temperature on initial rate of gas formation during disintegration of nitroglycering at 40-100°. 1) log $\frac{\Delta V}{\Delta\tau}$ [n cm^3/г min]

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[1] Results of investigations of disintegration of nitroglycerine in liquid phase at small degrees of filling and the higher temperatures are presented in the preceding article of the present collection.

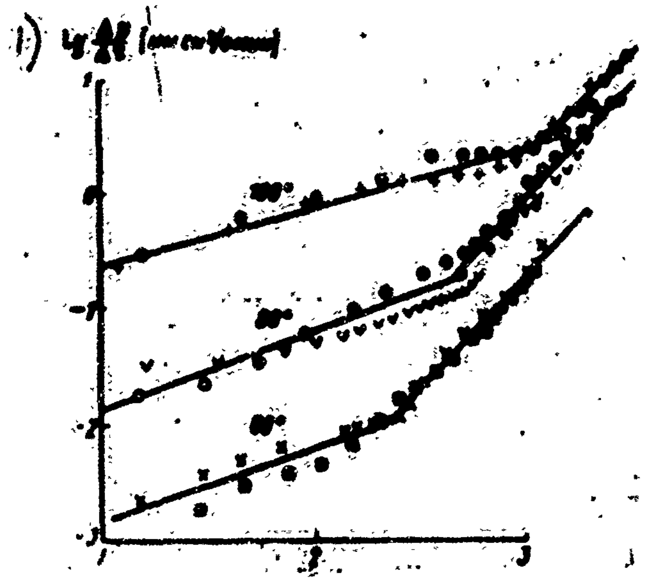

Fig. 4. Influence of pressure of disintegration products on rate of gas formation during decomposition of nitroglycerine (NG) at different temperatures. 1) log $\frac{\Delta p}{\Delta t}$ [mm cm^3/g min]

The comparatively small temperature coefficient of rate of gas formation in the first stage of decomposition of NG can be due to the change [specific gravity] of separate reactions in gas formation and, in particular, to the increase of the role of hydrolytic and oxidising reactions, the rate of which, apparently, depends less on temperature, than the rate of thermal disintegration. This promotes also large storage of products of disintegration in nitro ester due to high degree of filling reaction vessel.

After achievement of definite critical pressure of products of decomposition there begins a stage of sharp acceleration, analogous to disintegration at higher temperature. Fig. 4 represents the dependence of rate of change of pressure on the pressure of products of disintegration at 60, 80 and 100°. From graphs presented it is clear that the rate of gas formation in a section of sharp acceleration depends on temperature significantly less, than in the first stage. If activation energy, calculated by initial rates of gas formation, constitutes 29 kilocalorie/gram-molecule, then activation energy, corresponding to the second stage and calculated by rates at identical pressure of gasiform products is considerably less and constitutes 15 kilocalorie/gram-molecule.

Rate of gas formation in the second stage is proportional approximately to the second degree of pressure of products of decomposition. The presence of this dependence both at small δ and increased temperatures, and at large δ and relatively low temperatures allows us to make assumptions concerning the similarity of processes, proceeding at the stage of sharp acceleration in a wide range of temperatures (60-140°).

Magnitude of the critical pressure depends on temperature, being increased with the latter. Thus at 60, 80 and 100° critical pressure constitutes respectively nearly 250, 500 and 1000 mm of mercury. Comparison of these magnitudes with critical pressures, obtained during small degrees of filling shows that with increase δ from 0.1 to $\delta \approx 1$ critical pressure is increased 5-7 times (during small δ it constitutes for 80° nearly 70 and for 100° nearly 200 mm of mercury).

Significant growth of critical pressure during increase of degree of filling to its maximum magnitude can be explained by the fact that in the earlier stages of disintegration will be formed chiefly less active products of decomposition, as a result of which their pressure over nitro ester, necessary to transfer decomposition into second stage, should be higher. However it is possible to show that with certain assumptions the degree of filling of the reaction volume has to affect the magnitude of critical pressure during constant composition of the products of decomposition. If we assume that the products of disintegration are composed of gas accelerating disintegration and comparatively well soluble in nitro ester, and gases, not participating in disintegration and which are poorly soluble, then the critical pressure turns out to be the more common pressure of the products of disintegration, with which the pressure of the accelerating gas reaches definite and constant values for a given temperature (not depending on δ).

If we accept these assumptions, then the dependence of critical pressure on magnitude δ will be expressed by equation

$$P_{\text{кр}} = A + B\frac{\delta}{1-\delta},$$

where A and B are constant coefficients, depending only on temperature, during which A > B.

Consideration of this expression shows that at small degrees of filling (to $\delta = 0.3$) critical pressure remains practically constant and only at $\delta > 0.3$ with increase of the latter it is noticeably increased which in general agrees with the experiment.

The data obtained about disintegration of nitroglycerine permitted us to estimate influence of temperature on magnitude of induction period, during which time a definite quantity of gases were liberated corresponding to a pressure of nearly 1000 mm of mercury. With this pressure the disintegration of NG is characterized, independent of the temperature of the experiment, by a very high rate of gas formation and a large content in decomposition products of acid substances, quantity of which through titration by alkali of aqueous extract corresponds to their concentration in nitroglycerine (in conversion to nitric acid) in the order of percent.

Fig. 5 illustrates influence of temperature on duration of induction period for experiments with different degrees of filling of reaction vessel (both with maximum, and with lesser values of δ) in a wide range of temperatures (60-140°).

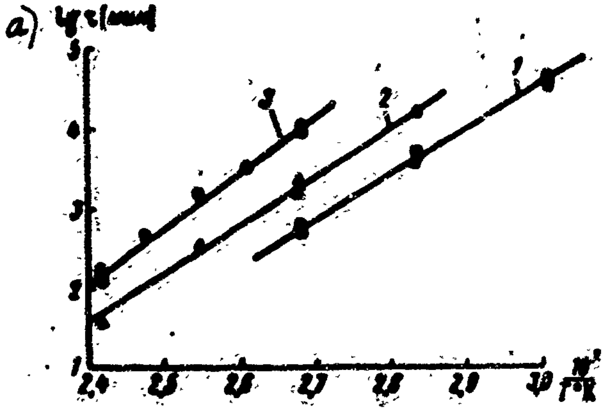

Fig. 5. Influence of temperature on induction period of disintegration of nitroglycerine at different degrees of filling of reaction vessel. a) log τ /min/

1) $\delta \approx 1$, 2) $\delta \approx 0.03$, 3) $\delta \approx 0.006$.

This dependence for studied δ is described by equation $\tau = Ae^{\frac{E}{RT}}$ and in coordinates $\lg\tau - \frac{1}{T}$ is expressed by straight lines. Straight line 1 shows dependence of induction period on temperature for disintegration of nitroglycerine at maximum degree of filling of reaction vessel at a range of 100-60°. Magnitude E, found by tangent of angle of inclination of this straight line, constitutes 26 kilocalorie/gram-molecule. It is near the magnitude of activation energy, calculated by initial rates of gas formation.

Magnitude E, received from experiments with $\delta \approx 0.03$ in a range of temperature 80-140° (straight line 2) constitutes 23 kilocalorie/gram-molecule and with $\delta = 0.006$ at 100-140° 32 kilocalorie/gram-molecule (straight line 3).

The data presented show that the temperature dependence of the induction period during disintegration of nitroglycerine in the presence of decomposition products is influenced by the degree of filling of reaction vessel, and also apparently, by the temperature range, inasmuch as with an increase of δ and lowering of temperature, E decreases from 32 to 26 kilocalorie/gram-molecule.

The results obtained allow us to estimate the behavior of nitroglycerine under the conditions of its storage.

Extrapolation shows that duration of induction period of disintegration of nitroglycerine at 20° under the conditions, when products of decomposition are almost completely/ /in nitro ester, constitutes 17 years. However, if products of disintegration have the opportunity, to this or that degree, to leave the condensed phase, then the induction period becomes correspondingly more. At $\delta \approx 0.03$ the induction period for 20° constitutes nearly 100 years. Further decrease of degree of filling of reaction vessel to 0.006 increases induction period to 2200 years. With comparison of these magnitudes one should consider that during the time of induction period a different degree of disintegration is attained depending upon magnitude δ. If one were to take in all cases quantity of gasiform products during full disintegration of nitroglycerine $v_0 = 600$ cm^3/g then during $\delta \approx 1$ the degree of disintegration will constitute nearly 0.2% [1]; during $\delta \approx 0.03$ nearly 3% and during $\delta \approx 0.006$ nearly 17%. It is necessary to indicate that such estimation of degree of disintegration at least for experiments with maximum δ is very conditional, in view of significant content of acid products in nitroglycerine at the stage of sharp acceleration, which was already mentioned above.

With magnitudes of induction period, obtained for 20° in presence of products of disintegration, it is possible to compare results of extrapolation of Robertson's data [5] for decomposition of nitroglycerine under the conditions of compulsory removal of gasiform products of disintegration by a flow of CO_2. It turns out that in these conditions the degree of disintegration 0.2%, corresponding to an induction period at $\delta \approx 1$, must be attained within 3000 years; degree of disintegration 3%, corresponding to induction period at $\delta \approx 0.03$, -within 50,000 years and, finally degree of disintegration 17%, corresponding to induction period at $\delta \approx 0.006$, -within 300,000 years. Shown magnitudes are incomparably larger than those, which ensue from results of experiments on disintegration of nitroglycerine in presence of products of decomposition.

Conclusions

1. The decomposition of nitroglycerine at low temperatures (40-100°) is studied.

2. It was shown that decomposition of nitroglycerine with these temperatures proceeds qualitatively similarly with disintegration of nitroglycerine at higher temperatures(80-140°). This similarity lies in the presence of two macroscopic stages, critical pressure and approximate proportionality of rate of gas formation in second stage to square of pressure of products of disintegration.

3. It is also shown that along with known similarity is quantitative distinction in disintegration of nitroglycerine during low and during high temperatures. Temperature dependence of initial rate of gas formation during low temperatures is expressed more weakly. In the second stage of decomposition critical increment of rate of gas formation constitutes nearly 15 kilocalorie/gram-molecule differing from high temperatures, where the rate of gas formation in second stage virtually does not depend on temperature.

4. An estimation is made of the magnitude of induction period of disintegration of nitroglycerine at 20°. The results obtained are compared with the influence of the degree of filling of reaction vessel on the possibility of removal of gasiform products of decomposition from nitro ester.

5. Peculiarities of decomposition of nitroglycerine at low temperatures are considered in an assumption about the increase in the first stage of disintegration of "specific gravity" of reactions of hydrolytic and oxidizing character with a relatively small temperature coefficient of rate, predominant in the second stage.

6. Developed is a methodology of study of thermal disintegration of explosive substances at a maximum degree of filling of reaction vessel, allowing us to widen the investigated range of temperature in the area of lower temperatures.

The authors express gratitude to K. K. Andreev for his considerable instruction during discussions of the work and the formulation of its results.

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Article No. 13 Chapter 2

Pages 197 - 207

V. V. Gorbunov and B. S. Svetlov

13. Influence Of Water And Acid On Self-Accelerated Disintegration Of Nitroglycerine.

Thermal decomposition of nitroglycerine in liquid phase in the presence of products of disintegration is a diphasic process, [3]; [5]. The first stage the induction period, is characterized by a comparatively small and slowly increasing rate of decomposition; the second stage proceeds with great self-acceleration. The duration of the induction period is influenced by the conditions under which the experiment was conducted. Different impurities, in particular water, acid, nitrogen peroxide, accelerate decomposition, reducing this period.

Water has an especially strong influence and to an even greater degree water with acid or with nitrogen peroxide, forming acid during interaction with water [1]. This allowed us to make assumption about the leading role of hydrolytic processes, taking place during decomposition of nitroglycerine both in the presence of water and acid, and during self-accelerated disintegration of nitro ester without additions [5].

Experiments, conducted at their own time to study the influence of water and acid on decomposition of nitroglycerine, do not give quantitative presentations on the role of concentration of impurities and temperature of experiment, since results of these experiments were received by manometric method or by method of flash in ampules [4] during a small ratio of volume of nitro ester to volume of ampule. Therefore a significant and sometimes indefinite part of the impurities and products of disintegration was in the gas phase and a quantitative estimate of their composition and role in the process of decomposition of nitro ester could be performed only by taking into account processes of diffusion and dissolution, which was not possible under the conditions of the experiments. Besides these experiments were conducted during relatively high temperature (mainly at 100° and above) in a narrow range which by itself hampered extrapolation of results at the lower temperatures, of interest to the practicians.

In connection with this experiments were set up with application of manometric method at practically full filling of volume of ampule of nitro ester which allowed us to trace decomposition of nitroglycerine in the presence of water and nitric acid (both separately and together) at a range of 40 – 100°.

Dosage of water and acid was realized by freezing out definite quantities of their vapor in reaction vessel with nitro ester, preliminarily liberated from volatile substances by means of exhaust. Accuracy of dosage, checked by "empty" experiment (without nitroglycerine), constituted ± 3%.

Experiments on decomposition of nitroglycerine at 100° and maximum degree of filling of vessel δ showed (fig. 1) that in the presence of 0.2% weight of water the acceleration of disintegration sets in significantly faster (approximately 1.5 times), than in the presence of the same quantity of nitric acid, and 2.5 times faster, than individual nitro ester.

An analogous result is received at lesser δ (0.03) in the presence of 0.5% weight of water. In this case acceleration sets in 3 times faster, than in experiment with the same quantity of nitric acid. It is necessary to note that the pressure – time curve in case of decomposition of nitroglycerine in the presence of water at $\delta \approx 1$ has the same character as at small δ, namely: the period of constancy of pressure, its temporary decrease (small) and subsequent sharp acceleration of gas formation. The time to the beginning of pressure decrease is somewhat less than that, which is observed at small δ and equal pressure of the vapor of the added water.

The character of the pressure - time curve in the experiment with nitric acid, attracts attention because it is saturable in the beginning. Apparently, the decomposition of nitric acid itself is superimposed on the disintegration of nitroglycerine in this period.

Fig. 2 and 3 present curves of decomposition of nitroglycerine in the presence of water and nitric acid at 60 and 40°.

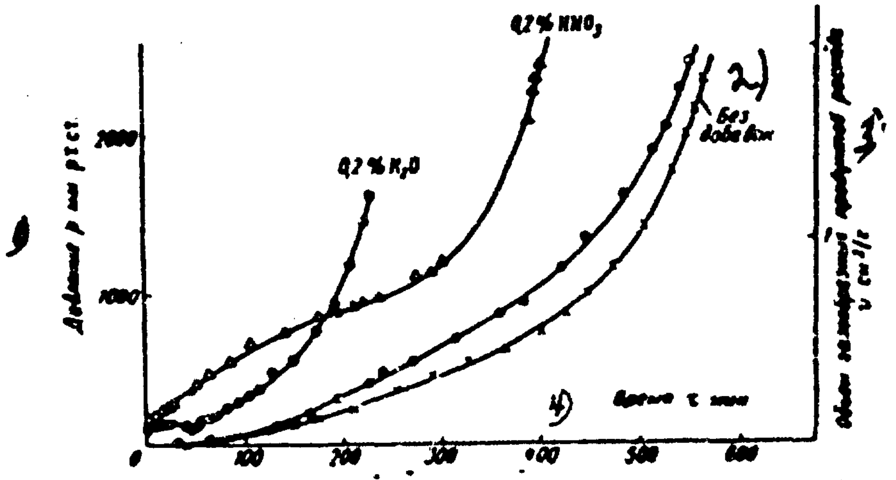

Fig. 1. Influence of water and nitric acid on decomposition of nitroglycerine at 100°. (For NG without additions curves of two parallel experiments are presented.) 1) Pressure mm of mercury; 2) Without additions; 3) Volume of gasiform products of disintegration $V\ cm^3/g$; 4) Time τ minute.

As can be seen from graphs, at 60° and definite contents of water disintegration of nitroglycerine is accompanied by characteristic drop in curve $p=f(\tau)$. Disintegration in the presence of 100% nitric acid proceeds on the curve usual for nitroglycerine. At first pressure increases slowly, then at the expiration of the induction period gas formation is accelerated abruptly.

Experiments showed that adding water or nitric acid to nitroglycerine significantly reduces induction period as compared with disintegration of dry pure nitroglycerine not only at increased, but also at low temperatures. However in the latter case, nitric acid by its own accelerating action, significantly exceeds water. At 60° the induction period for pure nitroglycerine constitutes nearly 600 hours, with addition of 0.2 and 0.4% weight of water it

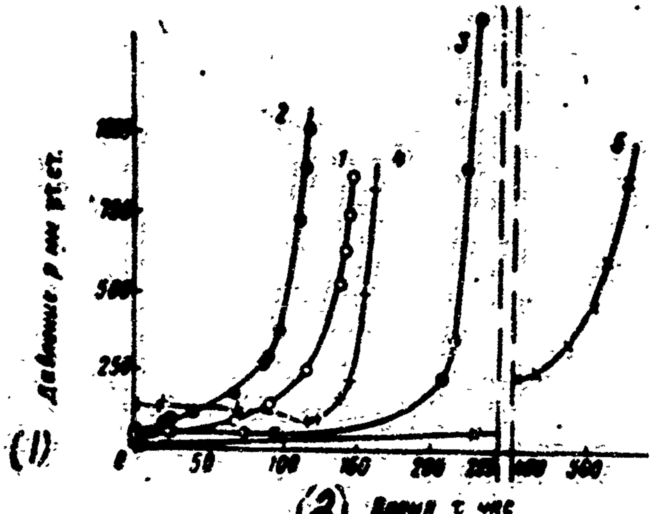

Fig. 2. Influence of water and nitric acid on decomposition of nitroglycerine at 60°. 1) 0.14% weight of 100% HNO_3, 2) 0.45% weight of 100% HNO_3, 3) 0.18% H_2O, 4) 0.42% of H_2O, 5) Without additions. (1) Pressure mm of mercury; (2) Time τ hour.

constitutes 230 and 160 hours respectively. In presence of 0.14% weight of nitric acid a sharp acceleration starts in 150 hours, and in experiment with 0.45% weight of acid, in 120 hours.

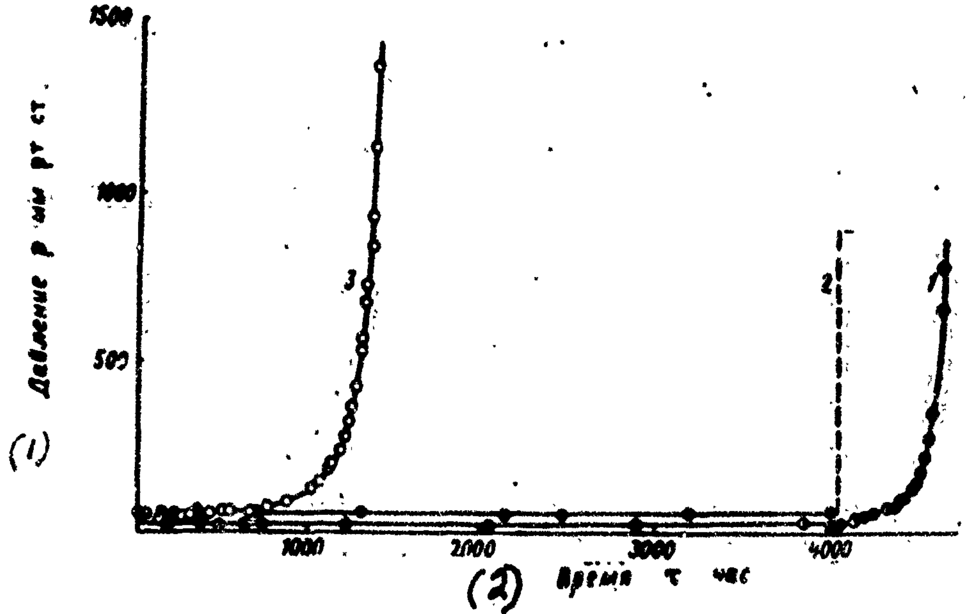

Fig. 3. Influence of water and nitric acid on decomposition of nitroglycerine at 40°. 1) 0.16% weight of H_2O, 2) 0.34% of H_2O, 3) 0.17% weight of 100% HNO_3. (1) Pressure mm of mercury; (2) Time τ hour.

Thus, at 60° water (0.2% weight) reduces time of induction period of disintegration of nitroglycerine approximately 2.5 times whereas nitric acid even in smaller quantity (0.14% weight) decreases this time 4 times. The ratio of the duration of the induction period with disintegration of the given nitro ester in the presence of water to the duration of this period for a product, containing acid, constitutes nearly 1.5.

At 40° nitric acid has an even stronger influence that at 60°. In connection with the fact that experiments with waterless nitroglycerine at 40° were not brought to sharp acceleration of disintegration due to their great durations, straight data on the influence of water on the induction period in these conditions are absent. An indirect method, based on extrapolation of temperature dependence of duration of induction period of a waterless product with 100, 80, 60° gives a magnitude of about 1 year at 40°. The ratio of this magnitude to time of induction period of disintegration of humid nitroglycerine constitutes about 2, which is nearly the ratio at 60°.

Experiments show that the induction period at 40° in the presence of 0.17% weight of acid constitutes 1300 hours, but at 0.16% weight of water it equals 4600 hours, i. e. acid reduces the time to the beginning of sharp acceleration of disintegration of nitroglycerine as compared with water 3.5 times, whereas at 60° this period was reduced only 1.5 times.

Thus, with lowering of temperature the accelerating influence of nitric acid on disintegration of nitroglycerine grows, the influence of water remains, apparently, constant. Accelerating action of acid is developed from the very beginning of the experiment. Initial rates of gas formation[1] in the case of addition in nitroglycerine of nitric acid are increased at 40 and 60° 5-10 times depending upon quantity of added acid. In experiments with water the pressure in a significant section of disintegration virtually does not grow. In experiments with moderately diluted acid initial disintegration rate is lower, than in the case of concentrated, but still higher than for individual nitroglycerine.

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[1] This rate was calculated as average on a section of disintegration from its beginning to separation of a quantity of gases, corresponding to 50 mm of mercury above equilibrium pressure of addition.

In the presence of diluted acid (to 20% HNO_3) pressure in the beginning for a long time either does not grow at all as in the case of experiments with water), or grows with a rate, less for nitroglycerine alone.

Increase of initial rate of gas formation in the presence of strong nitric acid, accompanied by sharp reduction of induction period, is conditioned, apparently by the development of oxidizing processes, the greater the specific value of which, the lower the temperature and the stronger the acid. Oxidizing reactions lead to the formation of poorly condensed products, and also water, participating in hydrolytic decomposition of nitroglycerine. In case of diluted acid, whose oxidizing action is not so great, hydrolysis proceeds mainly with the formation of nitric acid easily soluble in nitro ester. In this case, pressure either grows weakly (when specific gravity of oxidizing reactions are still significant) or does not grow at all.

In the presence of water alone pressure for a prolonged time remains constant due to the same causes which also exist at high temperature and small degrees of filling of reaction vessel. Hydrolysis of nitroglycerine is developed very slowly due to the neutrality of the medium. When as a result of disintegration and hydrolysis of nitro ester a certain quantity of acid is stored, hydrolysis is strongly accelerated due to abruptly expressed autocatalysis of this process. In known conditions is observed even a lowering of pressure, characteristic for experiments with water.

Thus, experiments showed that general rules of disintegration of nitroglycerine at increased temperatures in presence of water and acid are kept also at low temperature. However in these conditions the influence of the indicated substances is developed quantitatively otherwise.

The above described rules were fixed by results of experiments, in which to nitroglycerine was added water or nitric acid mainly in quantity about 0.2% weight.

For the purpose of exposing the influence of a quantity of water on disintegration of nitroglycerine corresponding experiments were conducted at 60°[1].

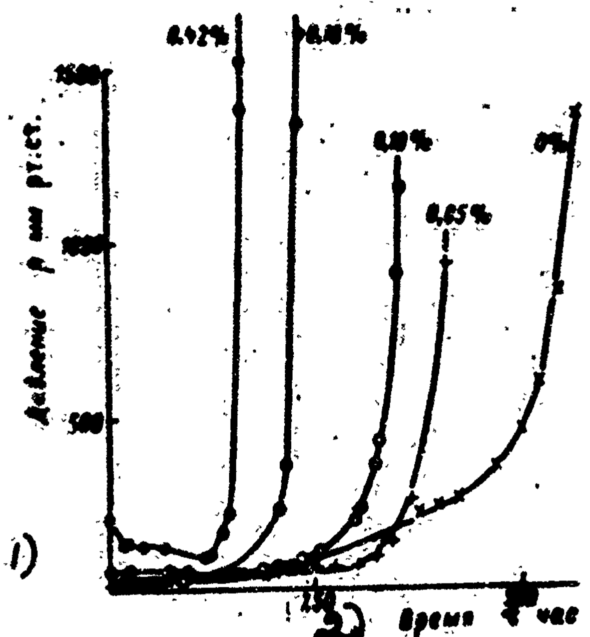

Fig. 4. Influence of a quantity of water on decomposition of nitroglycerine at 60°. Numbers by curves - contents of water in nitroglycerine at % weight. 1) pressure mm of mercury; 2) time τ hour.

Fig. 4 gives pressure - time curves for disintegration of nitroglycerine in the presence of different quantities of water. Addition to nitroglycerine of even 0.05% weight of water remarkably (approximately by 30%) shortens the induction period. Increase of water content leads to further reduction of this period. Thus, addition of 0.10% weight of water reduces time to beginning of sharp acceleration of disintegration of nitro ester by 40%, 0.18% weight of water - by 60% and 0.42% weight of water - by 70%. These data show that with increase of water content, its relative influence on the magnitude of the induction period, apparently, decreases. Pressure differing from experiments with waterless nitroglycerine in the beginning either grows very slowly (small water content), or remains constant throughout all the induction period. With an addition of 0.42% water the curve obtains the form with the characteristic drop usual for disintegration of humid nitroglycerine.

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[1] These experiments were carried out by M. S. Plyasunov.

At 40° (see fig. 3) also is observed a relative decrease of influence of the quantity of water. Thus, increase of water content twice (from 0.16 to 0.34%) leads to a reduction of the induction period from 4600 to 4000 hours, i.e. approximately by 10%. This is due to the fact that water along with active function (hydrolysis) also plays the role of diluent of the resulting acid that can lead to inhibition of both hydrolytic, and oxidizing reactions.

Influence of quantity of acid on disintegration of nitroglycerine is studied with application of HNO_3 of different concentrations. At 60° an increase in content of 100% nitric acid in nitroglycerine three times from 0.14 to 0.45% weight) shortened the induction period from 150 to 120 hour., i. e. by 25%.

Influence of quantity of 70-30% nitric acid on disintegration of nitroglycerine is shown in fig. 5. Here an increase in content of acid of the indicated concentration approximately 4 times reduces induction period by 70%.

Fig. 5. Influence of quantity of 70-80% nitric acid on decomposition of nitroglycerine at 60°. Numbers by curves - content of acid of given concentration in nitroglycerine in % weight. 1) Volume of gasiform products of disintegration V cm³/g ; 2) Time τ hour.

A similar influence is made by the change of acid content also at 40°. Increase of quantity of 70-80% nitric acid from 0.18 to 0.67% weight reduced the time of induction period from 1200 to 400 hours. (fig. 6). Further increase of quantity of acid to 2.5% weight reduced this time only to 300 hours. In this it is possible to see a certain similarity of influence of quantity of substances added to nitroglycerine, such as water or acid; relative reduction of induction period occurs with small quantities more sharply, than with large.

Especially we must note the fact that in the case of diluted acid, whose accelerating influence, as will be seen below, is most strongly developed, it is possible to observe its inhibiting influence if it is taken in a quantity, exceeding that necessary for saturation of nitro ester.

Fig. 6. Influence of quantity of 70-80% nitric acid on decomposition of nitroglycerine at 40°. Numbers by curves - acid content of given concentration in nitroglycerine in % weight. 1) Pressure mm of mercury; 2) Time τ hour.

Fig. 7 represents results of experiments on decomposition of nitroglycerine in the presence of 22-28% nitric acid. In one of them this acid was 0.19% weight (fully/ dissolved/), in another 1.9% weight so that part of it was not dissolved in nitro ester and was at a temperature of experiment in the form of suspension. In the first case the induction period constituted 80 hours; during the second, in the presence of a ten times greater quantity of acid, the time to sharp acceleration of disintegration constituted 280 hours and there was a significantly greater induction period in the experiment with 0.18% weight of water. Sharp acceleration of decomposition set in this case only after all acid was dissolved in nitro ester, which was judged by the disappearance of suspension. Before acceleration of disintegration there was observed a certain decrease of pressure. The inhibiting action established here is connected, apparently, with the fact that undissolved water, while extracting part of the acid, lowered thereby its contents in nitroglycerine, until it entered in reaction of hydrolysis or was dissolved because of increase of the general acidity.

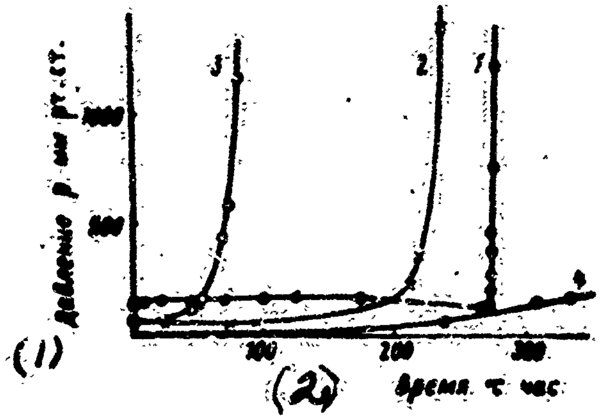


Fig. 7. Decomposition of nitroglycerine at 60° in the presence of 22-28% nitric acid, dissolved and partially undissolved in it, and dissolved water. 1) 1.9% weight partially undissolved HNO_3, 2) 0.18% weight dissolved water, 3) 0.19% weight dissolved HNO_3, 4) Pure nitroglycerine. (1) Pressure mm of mercury; (2) Time τ hour.

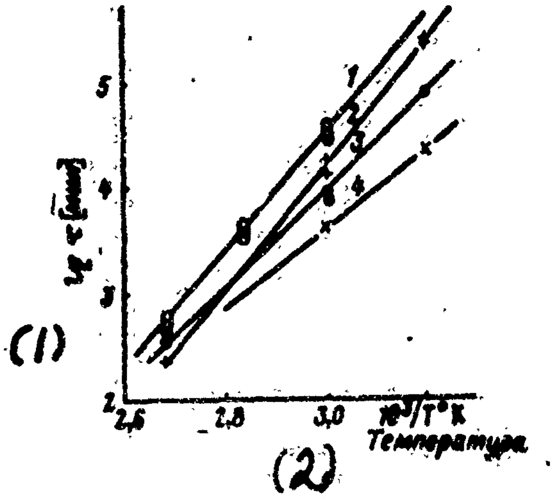


Fig. 8. Influence of temperature on duration of induction period during decomposition of nitroglycerine. 1) Pure nitroglycerine, 2) 0.2% weight of water, 3) 0.2% weight of 100% HNO_3, 4) 0.2% of 20% HNO_3. (1) lg τ [Min] (2) Temperature.

Results of experiments with addition of nitric acid and water, conducted in wide temperature range (100 - 40°), allowed us by extrapolation to estimate influence of these substances on induction period during storage of nitroglycerine in normal conditions (20°), when practically all products, both added to nitro ester, and formed during its disintegration, are in condensed phase.

Influence of temperature on duration of the induction period can be depicted in coordinates $\lg\tau - \frac{10^3}{T}$ by straight lines. In fig. 8 this dependence is presented for experiments with 0.2% of 100% nitric acid (straight line 3), for experiments with 0.2% of water (straight line 2) for pure nitroglycerine (straight line 1) and for experiments with 0.2% of diluted HNO_3 (straight line 4). Extrapolation shows that at 20° the induction period of disintegration of humid nitroglycerine constitutes 10 years, acid - 1.4 year, with addition of diluted nitric acid - 3 months waterless and neutral nitro ester - 17 years.

Thus, experiments show that water and nitric acid strongly affect the course of disintegration of nitroglycerine in the induction period stage significantly reducing it. In connection with this it is interesting to explain, whether these substances influence the rules of decomposition of nitroglycerine in the stage of sharp acceleration.

It was shown [5] that the rate of gas formation during disintegration of waterless pure nitroglycerine after the beginning of sharp acceleration, not dependent on the degree of filling of vessel, is proportional approximately to the square of the pressure of the products of decomposition. This rule is observed also in the case of disintegration in the presence of water and nitric acid of different concentrations at 40 and 60°. Fig. 9 and 10 present graphs of dependence of rate of gas formation on pressure of disintegration of products in logarithmic coordinates for experiments with water and nitric acid of different concentrations. As can be seen from fig. 9, at 60° points obtained can be described in general by a straight line, lying above the straight line for individual nitroglycerine. This points out the fact that at one and the same pressure of disintegration products in experiment in the presence of water or nitric acid the rate of gas formation is higher than in experiment with individual nitro ester. Tangent of angle of inclination for both straight lines constitutes

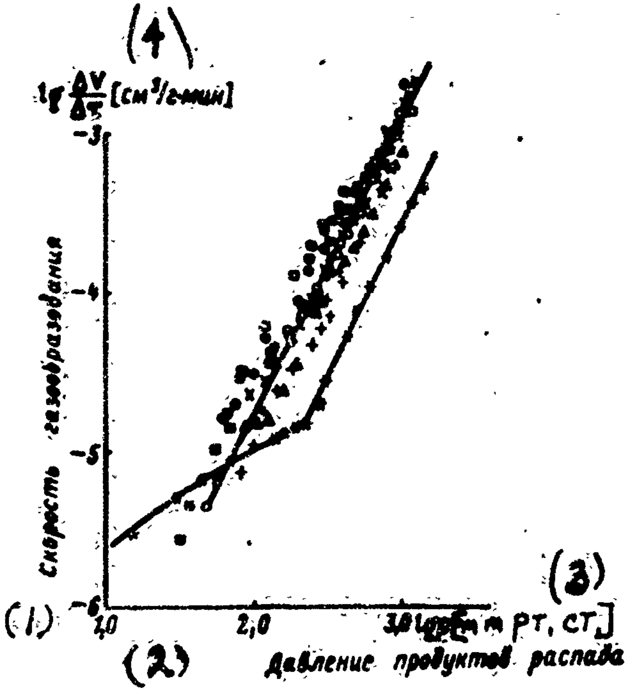
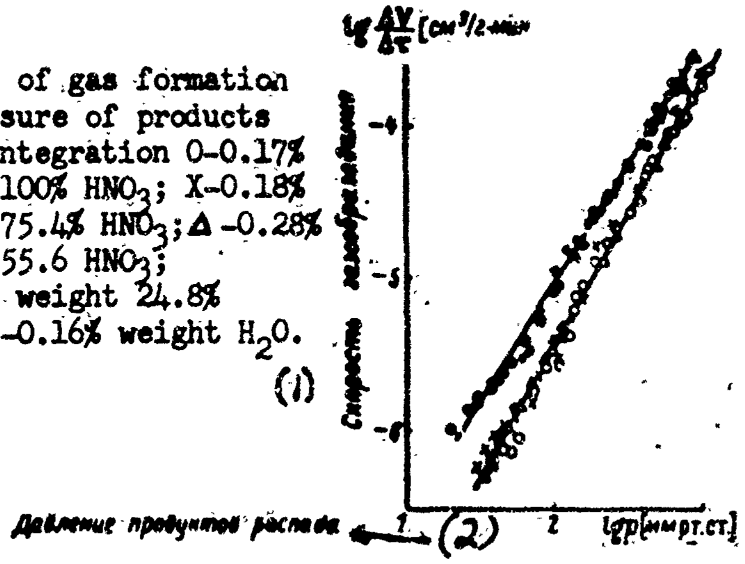


Fig. 9. Influence of pressure of disintegration products on the rate of gas formation during decomposition of nitroglycerine in the presence of water or nitric acid of different concentrations at 60°. * Pure nitroglycerine. 1) Rate of gas formation; 2) Pressure of products of disintegration. 3) mm of mercury; 4) (cm 3/g - min); O-0.14% weight 100% HNO_3; X-0.45% weight 100% HNO_3; +-0.27% weight 83.5% HNO_3; Δ -0.23% weight 77% HNO_3; ●-0.20% weight 41.5% HNO_3; ☐-0.19% weight 22.4% HNO_3; ■ = 0.1% weight H_2O;



1) Rate of gas formation
2) Pressure of products of disintegration 0-0.17% weight 100% HNO_3; X-0.18% weight 75.4% HNO_3; Δ-0.28% weight 55.6 HNO_3; *-0.22% weight 24.8% HNO_3; ●-0.16% weight H_2O.

Fig. 10. Influence of pressure of disintegration products on rate of gas formation during decomposition of nitroglycerine in the presence of water or nitric acid of different concentrations at 40°.

nearly 1.9. Inasmuch as at 40° experiments with a waterless substance were not brought to sharp acceleration, it is impossible to conduct such a comparison in this case. It is possible only to indicate the fact that data of experiments, broken down into two groups, are depicted (see fig. 10) also by straight lines with tangent of their angle of inclination nearly 1.7. The upper straight line corresponds to experiments with water and with diluted nitric acid, and the lower corresponds to experiments with 100% HNO_3. Consequently in experiments with water and diluted acid rate of gas formation was higher than in experiments with concentrated acid at one and the same pressure of products of decomposition. Observing the results of investigation at 60° one may also see, true, not so clearly that points, corresponding to experiments with water and diluted acid lie above points of experiments with concentrated HNO_3.

Thus, this data allows us to conclude that the role of water and nitric acid of different concentrations with their addition to nitroglycerine is limited mainly by the acceleration of those processes, which are prepared by the onset of the stage of sharp acceleration of disintegration of nitro ester. In this very stage they do not change the dependence of rate of gas formation on pressure of decomposition products, while increasing only somewhat the absolute rate of gas generation.

The hypothesis about the hydrolytic nature of the interaction of nitroglycerine with water during catalysis forming nitric acid [1] naturally assumes the presence of a certain optimum relationship of acid and water, with which the hydrolytic function of the latter is developed most abruptly. On the other hand, oxidizing action of nitric acid in the total process of disintegration of nitroglycerine also has to depend on its concentration.

Experiments conducted earlier showed that when adding water and acid together disintegration of nitroglycerine proceeds significantly faster, than in the presence of them separately. It was interesting to estimate the optimum relationship between water and acid in certain conditions. Muraour's experiment [6] points to the reality of such a relationship, according to the data of which nitrocellulose most quickly decomposes in the presence of 22% nitric acid, and also Samsonov's experiment [2], conducted at 100° in somewhat indefinite conditions and giving optimum ooncentration of nitric acid for disintegration of nitrocellulose 10%.

In our experiment disintegration of nitroglycerine was studied in the presence of about 0.2% weight of HNO_3 of a different concentration with a change of the latter in a range of 100-0%. As a characteristic of the action of substances added to nitro ester we took a ratio of the duration of the induction period, corresponding to the time of formation 0.8-1 cm 3/g gasiform products to the duration of the induction period in the experiment with 0.2% weight of water. Fig. 11 presents results of corresponding experiments, conducted at 60 and 40°. As can be seen from this graph, insignificant dilution by water of nitric acid to contents of the latter nearly 80% virtually does not affect duration of induction period at 60°. Further dilution abruptly reduces induction period and with the introduction into nitroglycerine of about 0.2% weight of 25-40% nitric acid it is lowered to a magnitude, two times less, than with concentrated acid and three times less, than in the case of water. Still more dilution entails an increase in the duration of the induction period.

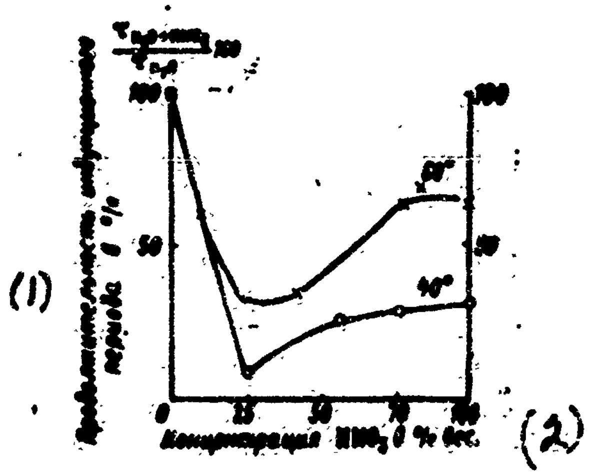


Fig. 11. Influence of concentrations of HNO_3 on duration of induction period of disintegration of nitroglycerine at 40 and 60°. 1) Duration of the induction period in %; 2) Concentration of HNO_3 in % weight.

A similar picture is observed also at 40°. Optimum concentration of nitric acid in this case is 25%. With this concentration of HNO_3 the induction period of disintegration of nitroglycerine is 3 times less than in the case of 100% nitric acids and 10 times less than in the case of water, added to nitro ester in a quantity nearly 0.2% weight. Examining these facts one should consider that nitric acid not only plays the role of catalyst of hydrolysis, but also is the oxidizer. Therefore optimum concentration of HNO_3, introduced into nitroglycerine, is a certain magnitude, totally reflecting its composition, optimum for each of the separate, processes, taking place in nitro ester.

Thus, the experiments conducted show that water and nitric acid develop their own accelerating action on disintegration of nitroglycerine, leading to a shortening of the induction period in all the studied range of temperatures (40-100°). However, if water affects disintegration at all temperatures to an approximately identical degree, the influence of nitric acid is abruptly increased with a lowering of temperature.

During disintegration of nitroglycerine complicated reactions take place of thermal and hydrolytic decomposition with participation of water added and formed with these processes. Hydrolysis is catalyzed by acid. Products of disintegration are oxidized by nitric acid and oxides of nitrogen formed during hydrolysis, or added nitric acid. Due to the complexity of the totality of these reactions it is difficult to definitely explain the rules obtained. The position is complicated still further by the fact that water fulfills not only the function of participant of hydrolysis, but by diluting acid, it thereby changes its oxidizing properties. On the other hand, nitric acid is not only a catalyst of hydrolysis and participant in the oxidizing reaction as a result of which water is formed, hydrolyzing nitro ester, but it is able to spontaneously decompose with the formation of water and oxides of nitrogen.

Examining results obtained in this work one should consider the change of"specific gravity" in the separate reactions in the general course of disintegration of nitroglycerine, and also temperature dependence of each reaction.

Conclusions

1. We have studied thermal decomposition of nitroglycerine in the presence of water, and also nitric acid of different concentrations at 40 - 100° under the conditions, where the substances added to nitro ester and the products of disintegration are practically completely dissolved in it.

2. It was shown that water reduces the induction period of disintegration of nitroglycerine at an approximately equal degree in all the studied temperature range, whereas nitric acid more weakly than water affects disintegration at high temperature and is significantly stronger than water at low temperature.

3. With the help of extrapolation we estimated the time of induction period at 20° for humid and acid nitroglycerine.

4. It was shown that at 40 and 60° the one most strongly reducing the induction period of decomposition of nitroglycerine was 25 - 40% nitric acid.

5. It was shown that water and nitric acid of different concentrations, introduced into nitroglycerine, influence mainly the processes, reducing the induction period. The stage of sharp acceleration of disintegration in

experiments with addition of water and HNO_3 shows the same regularities that exist with pure nitroglycerine.

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Tape No. MT-63-254

Pages 208 - 213 Article No. 14

B. S. Svetlov

14. On The Role of Nitrogen Dioxide In The Self-Accelerated Decomposition of Nitroglycerine

Nitrogen dioxide is one of the primary products of the thermal disintegration of nitro esters [6], [10]. In further stages of this disintegration it fulfills the function of oxidizer of the organic part of the molecule — this was established for example, on alkylimoncitrates [9] -- and, jointly with water (forming acid), the function of a catalyst of the hydrolytic disintegration of nitrate [1].

The role of nitrogen dioxide is especially essential in decomposition at relatively low temperatures, when its solubility in liquid nitro esters is great. The magnitude of solubility already was marked earlier [5], [11]; however, no quantitative evaluation of it was performed.

This work[1] is devoted to the determination of the solubility of nitrogen dioxide in one of the most practically important nitro esters - nitroglycerine.

For investigation nitroglycerine purified by double distillation in high vacuum, with $t^{*}_{m} = 12.9°$, was applied. Nitrogen dioxide was prepared by the decomposition of nitrate of lead with subsequent distillation of oxygen and drying by P_2O_5.

Two methods were used to determine solubility: weight and manometric. By the first method 100 - 150 mg of nitroglycerine were placed in the cup of quartz spring scales, suspended in a cylinderic vessel located in a thermostat. After

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[1] Student Yu. B. Dodonov took part in conducting the experiments.

evacuation nitrogen dioxide was admitted into the vessel; its pressure was maintained constant and controlled by a glass compensation manometer of the Bourdon type (see [2]) with an accuracy of ± 0.5 mm Hg. Dissolution was completed after approximately 20 min. The quantity of dissolved oxides of nitrogen was established with an accuracy ± 0.15 mg by the increase in weight of nitroglycerine. Volatilization of the nitro ester from the cup during the experiment did not occur; this was determined at the end of the experiment after exhausting of oxides of nitrogen.

By the second method about 1 g of nitroglycerine was placed in an ampule connected with a glass manometer, and, after thorough evacuation, a known quantity of nitrogen dioxide was introduced, with cooling by liquid nitrogen. Then the ampule was unsoldered from the installation and placed in a thermostat. Dissolution of nitrogen dioxide during energetic shaking of the ampule occurred after 5 min. The quantity of nitrogen dioxide dissolved in nitroglycerine was judged by the change of pressure, taking into account the equilibrium $NO_2 \rightleftarrows N_2O_4$ according to Bowdenistein [7][2].

The weight method was used to determine the dependence of the solubility of nitrogen dioxide in nitroglycerine on its equilibrium pressure. The determination was made during a change in the pressure of oxides of nitrogen from 100 to 900 mm Hg in the temperature interval of 20 to 80°.

Results of experiments show that the solubility of nitrgoen dioxide in nitroglycerine is proportional to its pressure in a degree of 1.5 - 2.3 (Fig. 1). With this there is observed a growth of this index with temperature.

Partial pressure of tetroxide of nitrogen in the equilibrium system NO_2 - N_2O_4 is approximately proportional to the general pressure of the mixture in a

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[2] Reversibility of dissolution was checked during subsequent heating and cooling of the ampule. Equilibrium pressures with this were reproduced with sufficient accuracy (± 1 - 2 mm Hg).

degree of 1.4 - 1.9. This allows to assume that under the experimental conditions is dissolved in nitroglycerine basically the tetroxide of nitrogen. In case of correctness of this assumption, the quantity of dissolved oxides of nitrogen, if their solubility corresponds to the law of Henry, should have been proportional to the partial pressure of N_2O_4 in an equilibrium gaseous mixture of oxides of nitrogen. In Fig. 2 is shown the dependence of solubility of N, expressed in molar fractions of tetroxide of nitrogen in nitroglycerine, from on the partial pressure of N_2O_4 calculated according to Bowdenistein [7].

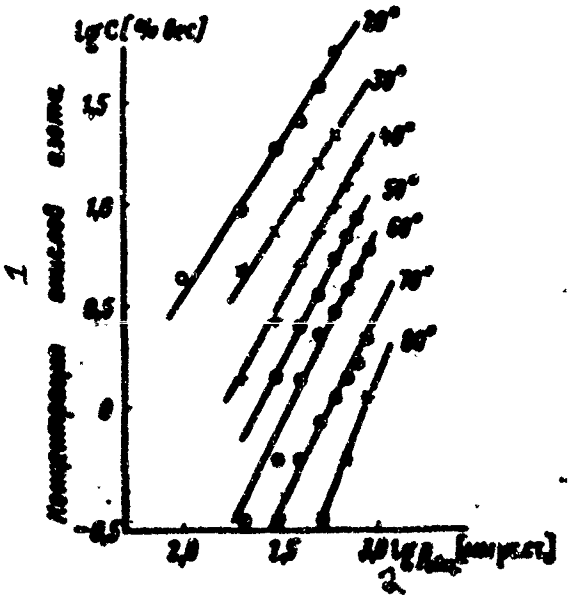

Fig. 1. Influence of general pressure of oxides of nitrogen on their solubility in nitroglycerine at different temperatures.
1) Concentration of oxides of nitrogen; 2) log P_{gen} [mm Hg].

The linearity of the connection of solubility with the calculated partial pressure of the tetroxide confirms the assumption that it is chiefly this tetroxide of nitrogen that is dissolved in nitroglycerine. At the same time, as can be seen from the graph, the influence of the pressure of N_2O_4 on its solubility corresponds to the law of Henry:

$$N = K \cdot PN_2O_4,$$

where N - concentration N_2O_4 in nitroglycerine in molar fractions; K - constant of solubility in mm^{-1}; PN_2O_4 - partial pressure of tetroxide of nitrogen in mm Hg.

Experiments were also conducted on the determination of the influence of temperature on solubility of nitrogen tetroxide in nitroglycerine, for which, at constant pressure of oxides of nitrogen, the experimental temperature was varied from 30 to 80°. Constants of solubility for each experiment in this case were calculated by the division of the general concentration of oxides of nitrogen in the solution in molar fractions of the tetroxide by its partial pressure in an equilibrium mixture.

The values of solubility constants determined by the weight and manometric methods are shown in the table.

As can be seen from the table, the results obtained by the weight and manometric methods are in quantitative agreement.

Table

Dependence of solubility constant of nitrogen tetroxide in nitroglycerine (in $mm^{-1}\ 10^4$) on temperature

1 Метод определения	2 Температура °C							Давление окислов азота мм рт. ст. 3
	20	30	40	50	60	70	80	
Весовой 4	17,3	11,5	7,52	5,66	4,53	3,02	1,99	100—900*
		10,5	7,57	5,88	4,73	3,24	2.54	600**
		10,7	7,80	5,23	4,10	2,47	1,90	760**
Манометрический 5	16,3	10,8	7,52	5,27	4,01	2,83	1,90	611 (при 80) 7
	17,3	11,7	8,03	5,37	4,62	3,04	2,10	556 (при 80°) 7
Среднее значение 6	17,0	11,1	7,7	5,5	4,4	2,9	2,1	

1) Method of determination; 2) Temperature, °C; 3) Pressure of oxides of nitrogen, mm Hg; 4) Weight; 5) Manometric; 6) Mean value; 7) (at 80°).

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*Solubility determined at constant temperature and change of pressure. Constants are calculated by the method of least squares.

**Solubility determined at constant pressure and change of temperature.

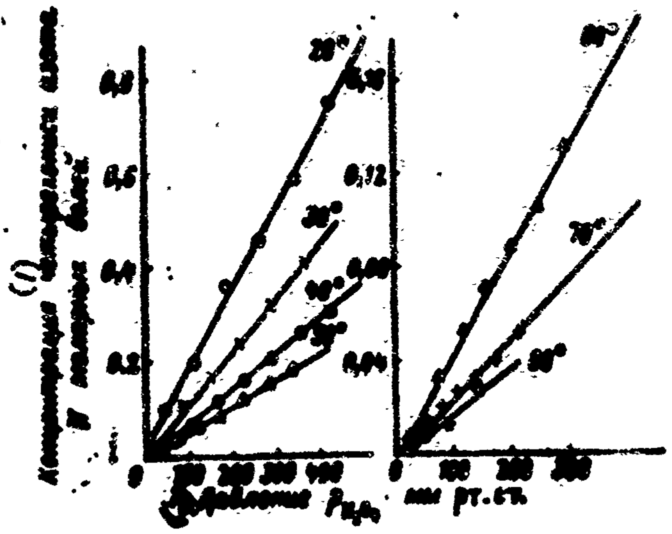

Fig. 2. Influence of partial pressure of N_2O_4 on its solubility in nitroglycerine at different temperatures.
1) Concentration of nitrogen tetroxide, N molar fractions; 2) Pressure $P_{N_2O_4}$ mm Hg

The dependence of the solubility constant of nitrogen tetroxide in nitroglycerine on temperature according to the data shown in the table to is expressed by the equation

$$\log K = \frac{3060 \pm 100}{RT} - 8{,}032.$$

On the basis of results the experiments conducted it can be concluded that in presence of an equilibrium mixture of NO_2—N_2O_4 nitroglycerine, under conditions of correctness for the given case of the law of Henry, dissolves chiefly the tetroxide of nitrogen. In other words, the equilibrium determining the relationship NO_2 and N_2O_4 in solution is displaced in the direction of the formation N_2O_4, which is in agreement with the determination of constants of the shown/equilibrium in a large number of organic solvents [8]. Thus, the contents of nitrogen tetroxide in nitroglycerine are proportional to its partial pressure or the general pressure of oxides of nitrogen to a degree of 1.5-2.

This conclusion can be compared with certain kinetic regularities established by us during investigation by the manometric method of the self-accelerated decomposition of nitroglycerine at 80-140° and of nitroglycol at 100° in the liquid phase. In the given conditions the speed of gas formation, growing slowly in the beginning of the experiment, starts to grow much faster after achievement of definite conditional critical pressure of gaseous products of disintegrations, proportional approximately to the second degree of pressure of gasiform products of decomposition. The value of the critical pressure, as can be seen from data to be mentioned later, is significantly increased with temperature.

Change of critical pressure during disintegration of nitroglycerine with temperature

t °C	δ*	1 $P_{кр}$ мм рт. ст.
80	0,006—0,06	60—80
100	0,0015—0,06	180—210
120	0,003—0,06	400—500
140	0,015	1000
140	0,029	800

1) Pcr, mm Hg.

It is natural to assume, proceeding from the presence of critical pressure, that a sharp acceleration of the decomposition of a nitro ester sets in only at the achievement, in the liquid phase, of a definite concentration of dissolved gasiform products of disintegration.

In a comparison of the indicated regularities of the self-accelerated decomposition of nitro esters with the influence of the pressure of oxides of nitrogen on the solubility of N_2O_4 in nitroglycerine, it is possible toconsider that sharp acceleration of disintegration is caused by the reaction in the liquid phase, with the participation of tetroxide of nitrogen. The speed of this reaction is proportional to the concentration or partial pressure of nitrogen tetroxide, and consequently to the pressure of an equilibrium mixture of oxides of nitrogen to a degree near to two.

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*Degree of filling of reaction vessel corresponds to the ratio of the volume of nitro ester to that of the ampule.

Inasmuch as the fraction of nitrogen dioxide in gasiform products of the decomposition of nitroglycerine at the achievement of critical pressure is approximately constant and constitutes about 40 - 60% [6], then the proportionality of disintegration rate to the square of the general pressure of gasiform products becomes clear.

If one were to allow that the established temperature dependence of solubility is correct in the region of elevated temperatures, then by extrapolation it is possible to estimate the concentration of nitrogen tetroxide in nitroglycerine which corresponds to critical pressure. This concentration in weight percent constitutes:

at 80° $0{,}1 — 0{,}4 \cdot 10^{-2}\%$; at 100° $0{,}3 — 0{,}8 \cdot 10^{-2}\%$;
at 120° $0{,}3 — 0{,}8 \cdot 10^{-2}\%$; at 140° $0{,}4 — 1{,}2 \cdot 10^{-2}\%$.

In examing these values, it is necessary to consider the relatively limited amount of data about the contents of nitrogen dioxide in gasiform products of disintegration at the attainment of critical pressure, and also the possible influence on the solubility of N_2O_4 of other products of decomposition, which was not determined.

Presence of critical pressure, apparently, is stipulated by the fact that in beginning of disintegration the concentration of tetroxide of nitrogen in nitroglycerine is small, and, consequently, the speed of the reaction in which it takes part is also small as compared with the primary reaction. The concentration of N_2O_4 in the liquid phase grows by the measure of decomposition of nitroglycerine and at attainment of critical pressure it reaches a value at which the reaction in which it participates starts to predominate over the primary one. Therefore at a known moment the disintegration rate becomes approximately proportional to the second degree of the pressure of products of disintegration.

In the given work we will not touch in detail the question of the mechanism of self-accelerated decomposition of nitroglycerine; however, the assumption about the leading role of nitrogen tetroxide does not contradict the hypothesis of the hydrolytic character of disintegration with subsequent interaction of intermediate products [3]. Indeed, according to the data of G. N. Bespalov [4], hydrolytic interaction of water with nitroglycerine in the presence of the acid formed with this proceeds very fast. If one were to proceed from this, then it is possible to consider that during the self-accelerated decomposition of nitroglycerine, when the quantity of NO_2 in products of disintegration is great and, consequently, the speed of formation of nitric acid is great, the speed of the hydrolytic reactions catalyzed by the acid is also great. Certainly, therefore, in the sequence of two processes one of which evokes the disappearance of water because of hydrolysis and the other its formation as a result of oxidation of organic products, the reaction controlling the speed of decomposition is the slower, i.e., oxidation. Assuming that during the decomposition of nitroglycerine oxidation proceeds basically with the participation of nitrogen dioxide, it is possible to expect that at the stage of sharp acceleration the speed of decomposition should be proportional to the concentration of N_2O_4, since the dioxide is joined in the tetroxide in solution. In such a case the disintegration rate should be proportional to the square of the general pressure of gasiform products of decomposition, which is confirmed by experiment.

Study of the thermal decomposition of nitroglycol showed that after achievement of a definite critical pressure of products of disintegration the speed of gas formation, as in case of nitroglycerine, becomes proportional to the square of pressure. Therefore it is possible to consider that the described scheme of self-accelerated decomposition of nitroglycerine applies also to the disintegration of nitroglycol.

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Chapter 2 Article No. 15

Pages 214-218

V. V. Gorbunov and B. S. Svetlov

15. On the Role of Condensation Products in the Disintegration of Nitroglycerine.

Thermal decomposition of nitroglycerine (NG) in certain conditions proceeds in two phases: after a relatively prolonged induction period there is a stage of sharp acceleration, characterized by fast growth of speed, which with this becomes proportional to approximately one square of pressure of gas products [2] [6]. Reduction of the induction period with increase of degree of filling of ampoule, the necessity of the presence of a certain "critical" pressure for transition of the first stage to the second, directs experiments on the action of gas products of disintegration on the decomposition of NG - all these observations confirmed the earlier expressed assumption [5] [7] about the fact that in the indicated acceleration a large, if not decisive role, is played by the products of disintegration, possessing high volatility. These products, apparently, are water, oxides of nitrogen and nitrogen containing acids. If the contents of them in NG attains a definite level, then as [1] [2] [3] [6] consider, this evokes sharply accelerated decomposition, conditioned by the hydrolytic and oxidizing-reduction interaction of the indicated substances with nitro esters or with products of its disintegration. However side by side with volatile substances in the course of decomposition of NG, apparently, will be formed also nonvolatile intermediate products [3], the possible influence of which on disintegration of nitroglycerine still has not been considered.

In this work an attempt was undertaken to show the presence of and to estimate the role of condensation products in the disintegration of NG. By the manometric method [3] we conducted decomposition of NG, after which the gaseous and easily-volatile products were removed and the decomposition of the remaining substance was studied. It turned out that removal of volatile substances from partially decomposed nitro esters occurs with very much difficulty and for its full completion it is necessary to apply a vacuum (residual pressure 10^{-4} - 10^{-5} mm Hg) in combination with a trap cooled by liquid nitrogen for the duration of several days. The completeness of removal of volatile products was controlled by the change of pressure in the disconnected pumps and trap. As the experiment showed, gas formation at decomposition of the substance received in this manner is characterized, first, by a very large initial speed, secondly, not by acceleration, but delay in time and, third, by the absence of the brown color of gas products with small contents of gases in them, condensed at room temperature (near 20%). Only significantly later, when sharp acceleration occurs, the gas phase was the color of nitrogen peroxide.

In first series of experiments NG initially was decomposed at a degree of filling of the vessel $\delta = 0.20$ and temperature 100° to a pressure of gas products 2800 mm Hg which corresponds to approximately 10% disintegration. After continuous evacuation of volatile substances[1] for the duration of three days, with this product the experiments were continued at 70 - 100° and $\delta = 0.03 - 0.04$. As can be seen from the results obtained (fig. 1), gas formation in time occurs on a saturable curve, which then changes into a straight line with a speed, many times exceeding the speed of gas formation at disintegration of fresh nitroglycerine on the first stage. If one were to conduct an experiment to large pressures (over 600 - 700 mm Hg at 100°), then the approach of sharp acceleration

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[1] In preparation of each experiment, an ampoule containing a product was preliminarily evacuated for not less than 24 hours.

of disintegration is observed.

On the speed of gas formation of partially decomposed NG the temperature influences significantly less, than at disintegration of fresh nitroglycerine, and the temperature coefficient leads to magnitude E in Arrhenius equation of nearly 20 kilocalories/mole.

In the second series of experiments NG was used, obtained by decomposition at $\delta = 0.24$ and temperature 100° with a degree of disintegration of about 7%. The insufficiently evacuated product, having at 90° an initial pressure of about 30 mm Hg, was decomposed on the saturable curve only the first 40 minutes after which a sharp acceleration of disintegration occured. A well-evacuated product (initial pressure approximately 8mm Hg) under analogous conditions (90° and $\delta = 0.04$) gave a curve of gas-formation identical to the one which was obtained in the first series of experiments.

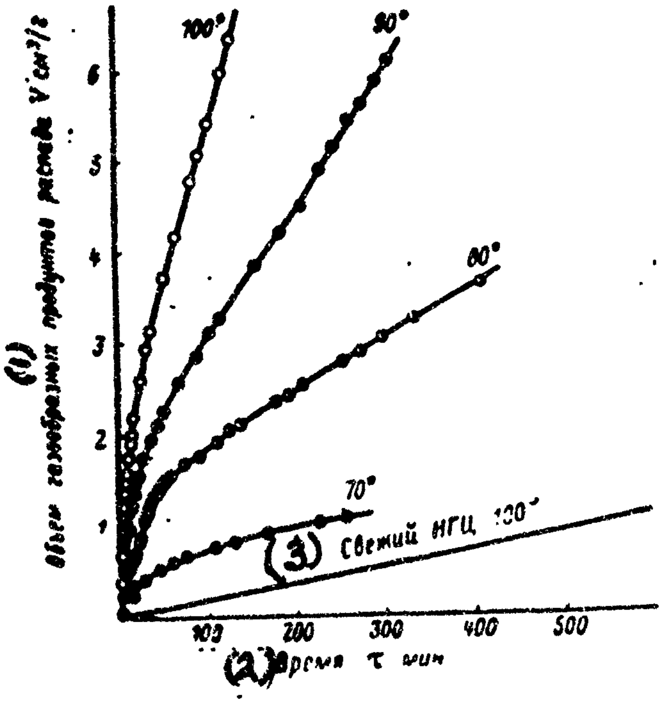

Fig. 1. Thermal decomposition of nitroglycerine with a 10% degree of disintegration after removal of gaseous and easily-volatile products from it in comparison with fresh NG (temperature of experiment 70 - 100°, $\delta = 0.03 - 0.04$). 1) Volume of gaseous products of disintegration V cm 3/g; 2) Time τ minutes; 3) Fresh NG 100°.

An experiment was undertaken to separate the condensation products[1], for which partially decomposed NG after thorough evacuation was poured in a supercooled state into a test tube, on the bottom of which were crystals of nitroglycerine and kept for one month at a temperature of approximately 0°. As a result of this the product was divided into two fractions; liquid and solid (in these conditions), which were used for further study of disintegration of NG. If thermal decomposition of the product before crystallization had a quantitative similarity with decomposition of the substance of the first series (see fig. 1), then the separated liquid fraction was decomposed significantly faster (approximately by 5 times). The substance of the solid fraction was decomposed at 110° with speed of gas formation and induction period, approximately corresponding to fresh nitroglycerine in these conditions (fig. 2).

Here are the results of experiments on disintegration at 90-110° of the liquid fraction of the substance, obtained after crystallization. At 100 and 110° pressure-time curves in the decomposition of this product throughout the entire experiment have a saturable character. However this dependence does not conform to equations of reactions of the first or the second order. Initial speed of gas formation of partially decomposed nitroglycerine is very great and approximately a thousand times more than the initial speed of gas formation in the disintegration of fresh nitroglycerine. At 90° decomposition in the beginning has the same character as at a higher temperature, but upon achievement of a certain pressure (near 1000 mm Hg) is accelerated. Addition of water to the liquid fraction of the substance in this case does not change the initial stage, but evokes sharp acceleration of disintegration significantly earlier. Besides these two series of experiments, separate experiments were

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[1] The presence of nonvolatile intermediate products in the disintegration of NG was confirmed by M. S. Plyasunov by depression of temperature of melting, which in the case of disintegration of this nitro ester $\delta = 0.02$ and 120° to 3% constituted 4°.

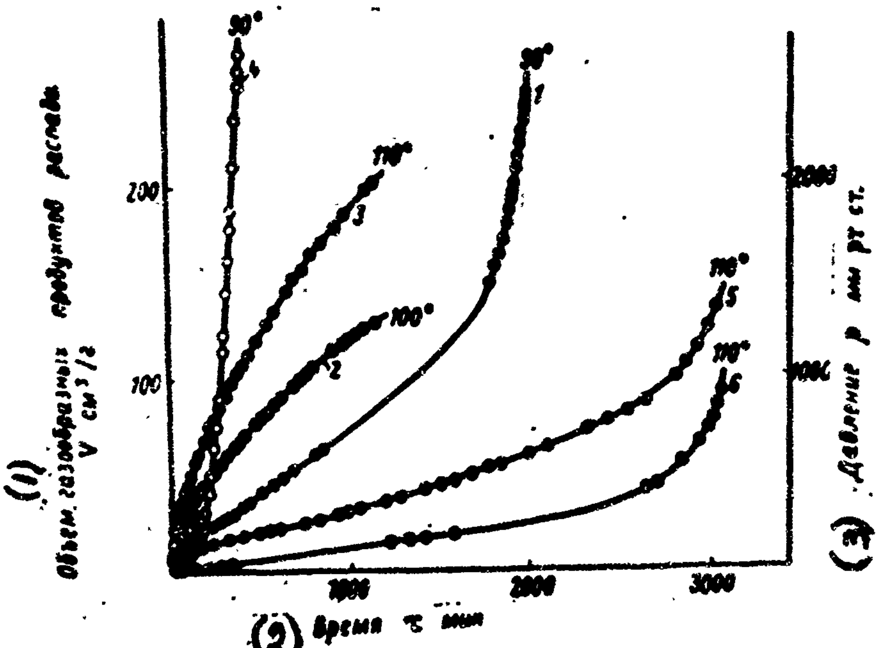

Fig. 2. Thermal decomposition of nitroglycerine with 7% degree of disintegration after removal from it of gaseous and easily-volatile products and crystallization, in comparison with fresh NG (temperature of experiments 90 - 110°, δ = 0.006). 1) 2) 3) Liquid fraction after crystallization; 4) The same, but with 1.7% by weight water; 5) Solid fraction after crystallization; 6) Fresh NG. (1) Volume of gaseous products of disintegration; (2) Time τ minutes; (3) Preasure p mm Hg.

conducted, which showed that the picture of disintegration of partially decomposed nitroglycerine, liberated at the stage of sharp acceleration from volatile products, does not depend on what nitro ester was initially applied: dry, wet or acid. Titrating by an alkali with phenolphtalein of the aqueous extract of partially decomposed NG after its thorough evacuation from volatiles showed that in the product there is nearly 1% acid in conversion to oxalic.

The totality of facts obtained can be explained if one were to proceed from the following positions. In the disintegration of NG intermediate difficultly-volatile products will be formed, significantly less stable at heating, than nitro ester itself. The content of these products is small and, apparently, does not exceed 10%, in accordance with the small degree of disintegration of NG under the conditions of our experiments. Decomposition of intermediate products leads to formation of substances of comparatively weakly accelerating disintegration of NG. Therefore, upon heating of partially decomposed NG gas formation in the beginning occurs basically as a result of disintegration of intermediate products. By measure of decrease of quantity of the latter, gas formation is delayed and specific gravity of gas formation is increased due to decomposition of NG.

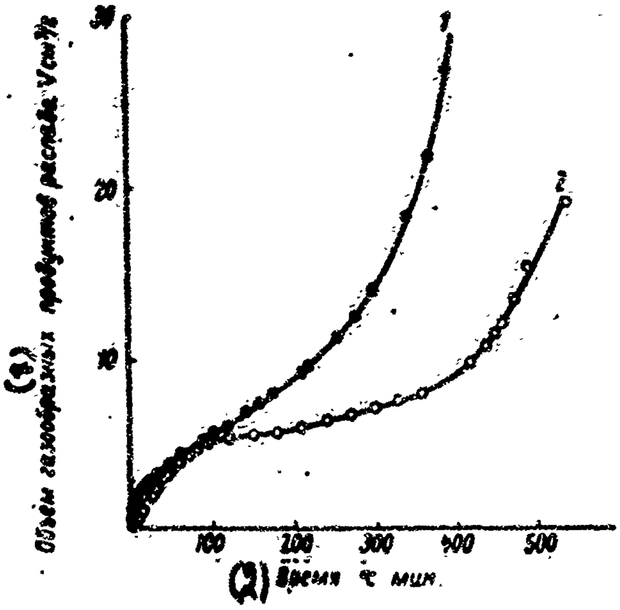

Fig. 3. Thermal disintegration of partially decomposed nitroglycerine, after removal from it of gaseous and volatile products in comparison with fresh NG in the presence of 0.7% by weight oxalic acid. (temperature of experiment 100°; [illegible] = 0.03). 1) Partially decomposed NG (from the first series of experiments); 2) NG with 0.7% by weight oxalic acid. (1) Volume of gaseous products of disintegration $V_{cm}3/g$; (2) Times τ minutes.

Further disintegration can lead to a self-accelerated process, determined basically by decomposition of nitroglycerine.

It is necessary also to note that the change of gas formation in time upon disintegration of partially decomposed NG takes place qualitatively similar with disintegration of fresh NG in the presence of oxalic acid (fig. 3), which, according to the data of G. N. Bespalov [4], on the initial stage proceeds with a great, but decreasing in time, speed, ten times exceeding the speed of gas formation in the disintegration of pure NG[1]. On the subsequent stage there is sharp acceleration of disintegration, and then the gas phase on a section to the beginning of this stage remains colorless. Addition of water to NG with a large

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[1] An analogous curve is obtained in the decomposition of diglycoldinitrate in the presence of oxalic acid.

quantity of oxalic acid leads to a picture of gas formation, qualitatively similar to that, which is obtained for disintegration of partially decomposed nitroglycerine in the presence of water. Thus, as under the conditions of thermal decomposition of NG, formation of nonvolatile acid is not excluded as a result of oxidizing-reduction reactions[1], such a similarity can not be limited only to the formal side.

Conclusions

1. Liberation of nitroglycerine decomposing at the stage of sharp acceleration from gaseous and easily-volatile products does not vindicate the initial picture of disintegration of nitro esters.

2. Gas formation in the disintegration of partially decomposed nitroglycerine after liberating it from volatile products proceeds with a very great speed which dimishes in time, the temperature coefficient of which is less than in the decomposition of pure nitroglycerine.

3. Disintegration of partially decomposed nitroglycerine is qualitatively similar with disintegration of this nitro ester in the presence of oxalic acid.

4. Thermal disintegration of partially decomposed nitroglycerine proceeds as if in it there were difficultly-volatile products, the constant of speed of decomposition of which significantly exceeds the constant of disintegration rate of the nitroglycerine itself.

5. In self-accelerated decomposition of nitroglycerine in the presence of products of disintegration, the speed of the process is determined not only by the easily-volatile products, but also, apparently, by the formation of nonvolatile intermediate products of decomposition.

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[1] Analysis of partially decomposed NG after removal of volatile products maintains the presence of nonvolatile acid in it.

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Tape No. MT-63-254 Article No. 16 Chapter 2

Pages 219--224

V. V. Gorbunov

16. On the Solubility of Water in Nitroglycerine

Water shows a strong accelerating action on the thermal decomposition of many nitro esters. This action, it is considered, is conditioned by its hydrolytic interaction with nitrates [1] [3] [5]. Naturally it is quantitatively connected with the contents of water in the nitro ester. Therefore for its detailed consideration and, in particular, for a more precise definition of the mechanism of the indicated interaction, it is necessary to know the solubility of water in nitro esters. This work is basically devoted to the determination of the solubilit of water in nitroglycerine (NG), by whose example the role of water in the decomposition nitro esters was studied in the most detail.

For the investigation we used NG purified by double distillation in high vacuum, with a melting temperature of 12.9°. Experiments were conducted by the manometric methodology [2] in the following form: in the ampule of a glass manometer of the Bourdon type with a volume of 10-12 cm^3 we placed about 0.5 g NG; after evacuation to full removal of volatiles a definite quantity water vapor was introduced into the ampule. For that we filled a glass sphere of known volume with water vapor and measured its pressure and temperature. The quantity of water in the sphere was calculated by data for superheated steam [4]. It was established that if into an evacuated ampule <u>not</u> containing NG we introduce water vapor with a ratio of pressure in the dosing sphere to the vapor tension of saturated steam at the same temperature of $p/p_s = 0.52 - 0.84$, then after holding in a thermostat at 100° a pressure was established in the ampule some 26 - 40% higher than the calculations would indicate. This, apparently, was stipulated by the adsorption of water on walls of dosing sphere, not taken into account under the experimental conditions. The magnitude of this adsorption, according to the data Mak-Ben [6], starts to increase abruptly at p/p_s larger than 0.6. In order to decrease the role of adsorption, the dosing sphere with water vapor is heated to a temperature of 60 - 100°. In connection with this the accuracy of measurement of water vapor pressure is increased simultaneously, owing to the growth of its absolute magnitude. As a result, the pressure of water vapor in the ampule without NG at the experimental temperature did not exceed the calculated by more than 1.0 - 1.5%. After the introduction of water the ampule was unsoldered from the installation and placed in a liquid thermostat. With energetic shaking of the ampule the dissolution of water in NG was completed after 10 - 15 min, which was determined by the establishment of a constant pressure. Proceeding from the equilibrium pressure of water vapor over NG and the general quantity of introduced water, we calculated its content in the condensed phase. The determination of solubility was made at temperatures of 30 - 90° in the interval of pressures from 16 to 120 mm Hg [1].

Inasmuch as the molar concentration of water in solution did not exceed 2%, and pressure of water vapor was significantly less than its value for the saturated state, it was assumed that the solubility of water in NG under the experimental conditions obeys the regularities of the solubility of gases in liquids. The solubility constant was calculated, in agreement with the law of Henry, by the division of the concentration of water in NG in the equilibrium pressure of its vapor.

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[1] Reversibility of dissolution was checked by subsequent heating and cooling of the ampule. The difference between equilibrium pressures obtained with this was no more than 2 mm Hg.

The biggest deviations in the results of parallel experiments from the mean values were at low and at high temperatures attained 10%; this, apparently was stipulated by the small absolute values of pressures in first case and by the flow of disintegration of NG in the second [1]. This, in a significant degree, was determined by the interval of temperatures selected for study. Dependence of constant of solubility on temperature is depicted in Fig. 1.

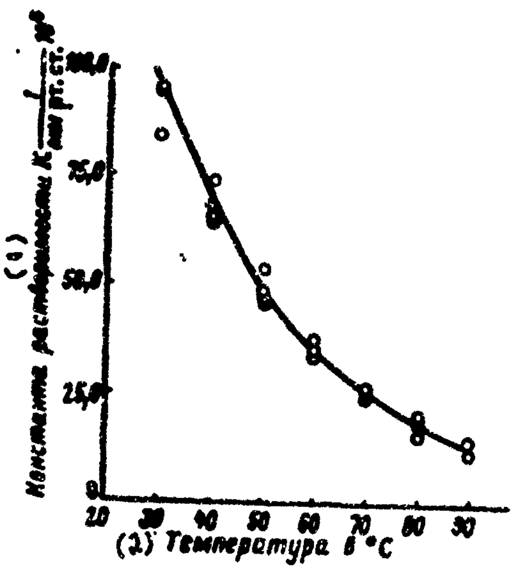

Fig. 1. Dependence of solubility of water vapor in nitroglycerine on temperature.

1) Solubility constant K (1/mm Hg) 10^6; 2) Temperature in °C.

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[1] Ratio of the equilibrium pressure of water vapor over NG to the vapor tension of saturated steam at the experimental temperature did not exceed 0.5, in consequence of which the influence of adsorption under the experimental conditions was insignificant.

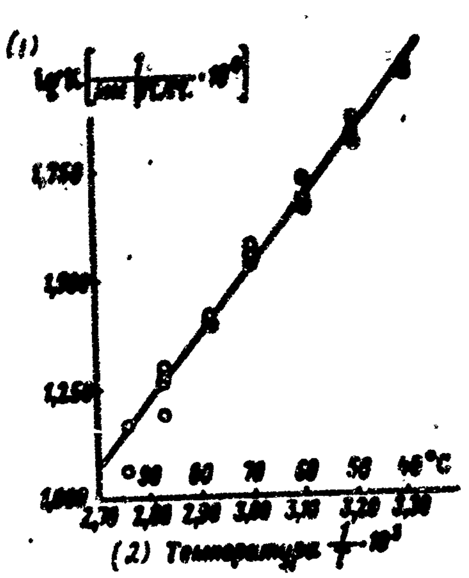

Fig. 2. Dependence of solubility of water vapor in nitroglycerine on temperature in coordinates log K - 1/T.

1) Log K [(1/mm Hg) . 10^6]; 2) Temperature, (1/T) . 10^3

This dependence can be expressed by a straight line in coordinates log K-1/T (Fig. 2) and by the equation $\log K = -9.114 + 1550/T$* corresponding to it. In the table (see below) are given the average experimental values of solubility constants and the results of extrapolating them at higher and lower temperatures. If we assume that the solubility of water in NG is subordinated to established regularities in the interval of pressures up to the vapor tension of saturated steam, then it is possible to estimate also the concentration of a saturated solution.

In connection with the fact that we also studied the influence of water on the thermal disintegration of diglycoldinitrate (DGDN) and dinitroglycerine (DNG), it turned out to be interesting to compare the solubility of H_2O in these nitro esters with its solubility in NG. In the interval of pressures from 23 to 240 mm Hg, the content of water in DGDN at 120° increases proportionally to the increase of the pressure of its vapor (Fig. 3), which indicates, in particular, the conformity of this dependence to the law of Henry.

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* Constants of this equation are calculated by the method of least squares.

The solubility constant of water for this nitro ester is somewhat less than for NG and equal $5.2 \cdot 10^{-6}$ mm^{-1}.

Table

Influence of temperature on solubility of water in NG

1- Температура в °С	20	30	40	50	60	70	80	90	100	120
2- Средние экспериментальные константы растворимости K в $мм^{-1} \cdot 10^6$	—	95	68	49	36	26	18	13	—	—
3- Расчетные константы растворимости K в $мм^{-1} \cdot 10^6$	150	98	68	47	34	25	19	14	11	6.6
4- Содержание воды в насыщенном растворе ее в НГЦ в % вес.	0,26	0,31	0,38	0,44	0,51	0,58	0,66	0,74	0,81	0.97

1) Temperature in °C; 2) Mean experimental constants K of solubility in mm$^{-1} \cdot 10^6$; 3) Calculated constants K of solubility in mm$^{-1} \cdot 10^6$; 4) Content of water in a saturated solution of it in NG, in % weight.

DGN has a significantly greater dissolving ability; the solubility constant of water in it at 120° equal $36 \cdot 10^6$ mm $^{-1}$.

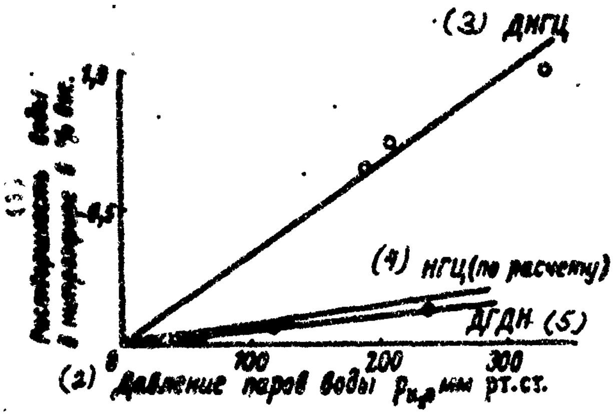

Fig. 3. Solubility of water in nitroglycerine, diglycoldinitrate, and dinitroglycerine at 120°, depending upon the pressure of its steam.
1) Solubility of water in nitro ester, in % weight; 2) pressure of water vapor, p_{H_2O}, mm Hg; 3) DNG; 4) NG (by calculation); 5) DGDN.

The latter circumstance should be considered in examining the experiments on the study of the disintegration of moist NG, since one of the products of reaction of hydrolysis, apparently, is DNG, whose presence can additionally increase the solubility of water in nitroglycerine.

Another product of the hydrolysis of NG, as G. N. Bespalov showed, is nitric acid, which can show an influence on the solubility of water in a nitro ester. Therefore in this work we estimated the solubility of H_2O in acid NG. The addition in the system NG - H_2O of one volatile component led to the necessity of analysis the gaseous and liquid phases for contents of nitric acid. The instrument for determination of solubility of water in acid NG (Fig. 4) was a combination of two glass manometers (1) of the Bourdon type, united by a vertical cock (2). In ampule (3) we introduced a sample of NG and evacuated the instrument to the removal of volatiles. After that we closed the vertical cock (2) and in vessel (4) measured out the water and nitric acid. Anhydrous nitric acid, containing no oxides of nitrogen, was obtained directly prior to the experiment by distillation from a mixture of nitric-acid potassium and concentrated sulphuric acid; we measured it out in the form of vapor [1], analogously as with water.

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[1] Accuracy of dosage was checked by titration and also by means of calculation according to law of state of ideal gases. Usually the error did not exceed 5%.

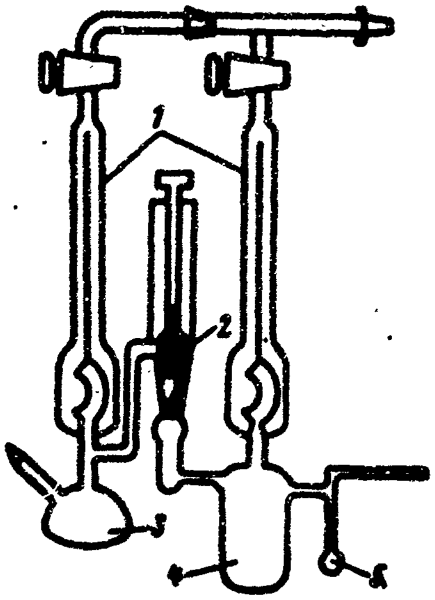

Fig. 4. Diagram of instrument for study of solubility of water vapor in acid nitroglycerine.

1) Manometers of Bourdon type; 2) Vertical cock; 3) Ampule for NG; 4) Vessel for water and HNO_3; 5) Ampule.

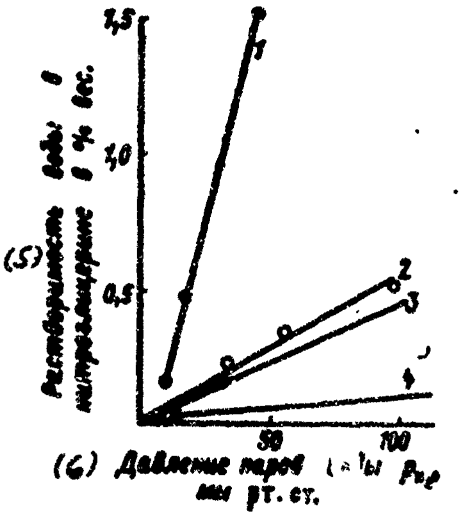

Fig. 5. Solubility of water in acid and neutral nitroglycerine at 50 and 100°, depending upon the pressure of its vapor. (Contents of HNO_3 in acid NG, 0.3 - 0.6% weight).

1) Acid NG at 50°; 2) Acid NG at 100°; 3) Neutral NG at 50°; 4) Neutral NG at 100°; 5) Solubility of water in nitroglycerine, in % weight; 6) Pressure of vapor $P\ H_2O$, mm Hg.

After the introduction of the additions the instrument was placed in a thermostat and the vertical cock was opened. As a result of the increase in the volume of the system and the solubility of water and nitric acid in NG a decrease in pressure occurred which continued usually, for 15 - 20 min. After the pressure drop ceased, we closed the vertical cock and extracted the instrument from the thermostat. Ampule (5) was cooled by liquid nitrogen and, after water vapor and HNO_3 were condensed in it, was unsoldered from the instrument. The content of HNO_3 in ampule (5) was determined by reverse titration and the pressure of its vapor over the solution at the experimental temperature was calculated according to the law of state of ideal gases. The pressure of water vapor over the solution was found by the difference between general and calculated pressures of HNO_3 vapor[1]. Thus we established the equilibrium composition of the gaseous phase over NG. The contents of water and acid in the NG were determined by the difference between the introduced quantity of the corresponding substance and the quantity of it in the gaseous phase. This methodology was applied in that case when, after determination of solubility, experiments were conducted on the thermal decomposition of acid NG in the presence of water, for which we used the glass manometer of ampule (3). If thermal decomposition did not occur, then we separated the liquid phase from the gaseous with the help of a system of cocks.

Solubility of water in acid nitroglycerine was determined at temperatures of 50 and 100° and contents of nitric acid in NG of 0.3 - 0.6% by weight. The dependence of solubility of water in acid NG on the pressure of its vapor is given in Fig. 5. Here for comparison are given lines 3 and 4, characterizing the solubility of water in a neutral product at the same temperatures. The content

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[1] For correctness of such a calculation it is necessary that the general pressure of the mixture of vapors of water and HNO_3 equal the sum of their pressures taken separately in the same conditions. As was shown by control experiments, this condition is fulfilled with an accuracy corresponding to that of the dosing.

of water in acid NG also increases proportionally to the increase in the pressure of its vapor. Comparison shows that the addition of HNO_3 to NG under the experimental conditions increases the solubility of water in the nitro ester by 5 - 7 times. Thus, nitric acid formed during the hydrolysis of NG fulfills the function of catalyst and oxidizer, and also promotes an increase in the content of water in the liquid phase and, consequently, hydrolysis.

Conclusions

1. The solubility of water in nitroglycerine at temperatures of 30 - 90° and in diglycoldinitrate and dinitroglycerine at 120° was determined.

2. The solubility constant of water in nitroglycerine varies in the given limits of temperature from $95 \cdot 10^{-6}$ mm^{-1} to $13 \cdot 10^{-6}$ mm^{-1}; the solubility constant of water in diglycoldinitrate is somewhat less ($5.2 \cdot 10^{-6}$ mm^{-1} at 120°), but in dinitroglycerine is much larger ($36 \cdot 10^{-6}$ mm^{-1} at 120°) than in nitroglycerine ($6.6 \cdot 10^{-6}$ mm^{-1} at 120°).

3. The solubility of water in nitroglycerine containing 0.3 - 0.6% by weight, of nitric acid is 5 - 7 times more than its solubility in a neutral product at the same temperatures.

The author expresses deep gratitude to Professor K. S. Svetlov for constant help in the work.

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Tape No. MT-63-254

Pages 225-240 Article No. 17

K. K. Andreyev

17. On the Thermal Disintegration of Nitroglycerine and the Possibility of Its Transition to Explosion

Nitroglycerine (NG) is the oldest and, till now, the most widely applied liquid nitro ester. Certain properties distinguishing nitro esters from substances of other chemical structure, for example nitro compounds and nitramines of the aromatic series, are expressed especially clear for NG. These peculiarities include slow chemical transformation, burning, flash and sensitivity to impact. Connected with each other in a known degree, they lead to the fact that the production of NG is the most dangerous of all secondary explosives.

The slow disintegration of NG, in certain conditions of its flow, can be extraordinarily strongly self-accelerated. This can cause a situation where, even at the low temperatures at which usually is conducted the industrial process, such high speeds of disintegration and heat emission are attained that strong local self-heatup sets in leading to thermal triggering of burning -- flash of NG. The burning of NG is unstable and is very inclined to transition to explosion; under the conditions of flash this inclination is expressed still more strongly.

We will consider in the present article the regularities of the thermal disintegration NG and those conditions which determine the possibility of triggering of flash as a result of the strong self-acceleration of this disintegration.

The speed of any chemical reaction depends on the temperature and, if the reaction proceeds in the gaseous phase or in solution, also on the concentration of reagents. In the case of the disintegration of liquid NG, if its products are gases, the concentration of the parent substance does not change and it is sufficient to consider only the dependence of reaction speed on temperature.

However, in real conditions the speed of the slow disintegration of NG depends also on time. This dependence is stipulated by two causes. First, the slow disintegration of NG is self-accelerated under the influence of products of the reaction. Therefore, if these products are not removed by one or another method, then their content in the NG increases and the speed of transformation grows correspondingly. Secondly, the disintegration of NG proceeds with the liberation of heat and, if this heat is not to diverted or is only partially diverted, then the temperature of substance grows and the speed of reaction grows correspondingly. Both factors of the self-acceleration of the process are interconnected: the greater the increase in the disintegration rate due to accumulation of disintegration products, the greater will be the speed of heat emission and, consequently, of thermal acceleration. The reverse dependence of chemical self-acceleration on thermal is somewhat more complicated, since at increased temperatures the products, which accelerate decomposition represent vapors and their solubility decreases with temperature; therefore, if these products have the possibility and time to depart, then the total acceleration turns out to be less than in the case when they remain completely in liquid.

It is necessary to consider also that a significant and complicated influence is shown on the development of chemical self-acceleration of the transformation of NG by those impurities which are either practically always(as water) in it or (as acid) can be contained in it with insufficiently thorough washing of the NG of spent acid.

Let us consider the more in detail both possibilities of the acceleration of NG disintegration - thermal and chemical.

Thermal Acceleration of the Exothermal Chemical Reaction to Explosion

During the course of exothermal chemical reaction, as a result of the liberation of heat; the temperature of the substance becomes higher than the ambient temperature. Therefore there occurs heat radiation from the substance to the environment. In Fig. 1 is represented the dependence of the heat income q_1 and heat outgo q_2 on temperature T.

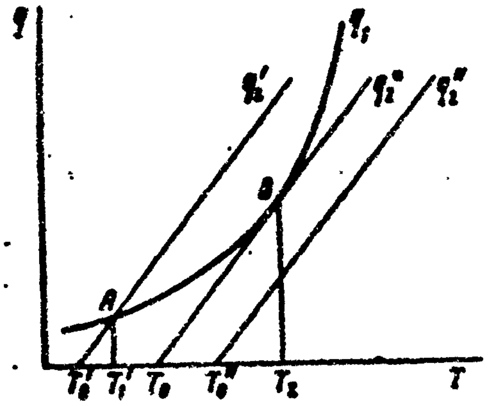

Fig. 1. Dependence of income (q_1) and heat outgo (q_2', q_2'', q_2^0) on temperature T.

If heat radiation is equal to heat income, then they are in equilibrium. Equilibrium is stable (point A) if the derivative of heat drain by temperature is larger than the derivative of heat income by temperature. This condition, as can be seen from the graph, is fulfilled if the temperature of the environment T_0' is relatively low. If it is higher (T_0'' or T_0), then the heat drain to the outside will become less and equilibrium between heat-income and heat outgo will not exist or it will be unstable, as for example, at point of contact B. A sufficiently small increase of temperature, so that heat-income becomes larger than heat outgo and self-accelerated growth of temperature sets in, will lead the transformation to speeds so high that we call it explosion.

The main factors of this process are the speed of the chemical transformation, its thermal effect, and the dimensions of the charge. The speed of heat emission is obviously proportional to the volume of the substance, and heat outgo -- to its surface. Inasmuch as the volume increases with the cube of the linear dimension, but the surface with its square, then it is clear that an increase in the dimensions of the charge will encourage the acceleration of the transformation and its transition to the region of instability.

D. A. Frank-Kamenetskiy [5] gave a mathematical analysis of the phenomenon for that case when heat transfer is accomplished by thermal conduction, and showed that the disruption of stability sets in if the dimensionless parameter

$$\delta = \frac{Q}{\lambda} r^2 B e^{-E/RT} \cdot \frac{E}{RT_0^2} \qquad (1)$$

becomes longer than a certain determined value dependent upon the form of the change and equal to 3.32 for a sphere, 2 for a cylinder, and 0.88 for a plane infinitely extended layer.

In formula (1):

Q -- thermal effect of reaction in cal/cm^3;

λ -- coefficient of thermal conductivity in cal/cm . sec . deg;

r -- radius of cylinder (sphere) or half-thickness of the layer, in cm;

B -- pre-exponential multiplies in Arrhenius' equation in sec^{-1};

E -- Activation energy, in cal/mole;

T_0 -- temperature of wall of vessel, in °K.

If the conditions lying at the base of this conclusion are fulfilled, i.e., if the speed of the reaction varies with Arrhenius' law and heat transfer occurs only through heat conduction, then by means of formula (1)it would be possible to calculate, for a given dimension of the charge, that temperature from which the slow transformation of decomposition to explosion will proceed, or to solve the reverse problem - to calculate for a given temperature, the minimum dimension of the charge which is the starting point for the transition of slow decomposition to explosion.

We shall carry out both computations. We will determine first, that minimum temperature of flash for a cylindrical column of NG 1 mm in radius. We will take the thermal capacity of nitroglycerine to be equal to 4.10^{-4} cal/cm·sec·deg. The thermal effect of transformation is taken equal to 800 cal/g, i.e. approximately half of heat of explosion. It is known that during slow thermal transformation the main part of the nitrogen is obtained in the form of endothermic NO; correspondingly, a part of the combustible elements remain incompletely oxidized and the thermal effect obtained is less than that during reaction to nitrogen, water and carbon dioxide. However, the magnitude of the thermal effect has a relatively weak effect on the result of the calculation. A decrease in Q of two times increases the calculated temperature of flash at E = 40,000 cal/mole by 5% in all. The Kinetic characteristic, taken according to R. Robertson [6], are E = 43,700 cal/mole, $B = 10^{1864}$ sec^{-1}.

Inserting in formula (1) the taken values of the parameters, we obtain

$$\frac{800\cdot 1.6}{4\cdot 10^{-4}}\,0,1^2\,10^{18,64}\,e^{-\frac{43\,700}{1,986T_0}}\cdot\frac{43\,700}{1,986T_0^2}=2.$$

From this t° = 163°.

For a charge with a radius of 0.5 mm an analogous calculation will find the critical temperature equal to 176°.

We see that the temperatures obtained are somewhat lower than the flash temperature of NG, determined usually by experimental methods (near 200°). The divergence is small and its physical meaning is clear. The viscosity of NG strongly decreases at increased temperatures, and heat outgo occurs in it not only by thermal conductivity, but also by convection, in particular as a result of mixing of the liquid by bubbles of emitted gases. This leads to an increase in heat radiation and, consequently, to an increase in flash temperature.

We will determine now, the dimension of a charge of NG required for its flash to occur at 20°.

Using formula (1), we write

$$\frac{800\cdot 1.5}{4\cdot 10^{-4}}\, r^{2}\, 10^{18.6}\, e^{\frac{-43\,700}{1.986\cdot 293}}\cdot\frac{43\,700}{1.986\cdot 293^{2}}=2.$$

Solving this equation, we obtain $r = 1.5 \cdot 10^{4}$ cm. Consequently for the decomposition of NG to be accelerated by means of self-heating to flash at room temperature, the radius of the charge should be more than 150 m, i.e., many times more than the dimensions those apparatuses, in which NG is obtained or stored in industrial conditions.

There is yet another side of the phenomen, whose calculation underlines the unreality of triggering of flash of NG under the considered conditions and prerequisites.

As can be seen from Fig. 1, the mutual location of the curve of heat income and the line of heat radiation is such that the difference between heat-income and heat outgo, which determines the speed of self-heatup decreases by the measure of temperature increase to the point of contact and only begins to increase rapidly at high temperatures. Calculation shows that the pre-explosion increase of temperature for a cylinderical charge constitutes 1.37 $\frac{RT_0^2}{E}$ degrees or for NG 1.37 $\frac{1,986\cdot 293^2}{43,700}$ = 5.35°. In order to estimate approximately the minimum time necessary for self-heatup of NG to 5.35°, let us assume that process proceeds adiabatically, i.e. without passing of heat to the outside. Warm-up to 5.35° with a heat capacity of NG of 0.35 cal/g · deg will demand 1.87 cal/g. During 100% decomposition of NG 800 cal/g will be emitted by our assumption; then for emission of 1.87 cal/g 0.234% must be decomposed of the NG. Constant of disintegration rate of NG at 20° is 1.1 · 10^{-14} sec^{-1}; therefore the time necessary for isothermal transformation of 0.234% of the NG will constitute 2.14 · 10^{11} sec or 7000 years. We see that even if there is a sufficiently large charge NG, in which flash can appear by means of thermal self-acceleration, in practice explosion will not occur, owing to its extremely large delay time.

Does, however, this conclusion signify that in real conditions triggering of flash of NG at low temperatures is impossible?

To this question one should give a negative answer. What form of slow decomposition can be developed to flash?

Above we noted that the slow chemical transformation of NG, if its gasiform products are not removed from the liquid, is developed with self-acceleration. This chemical self-acceleration in the case of NG, and in known conditions also during the decomposition of other nitro esters, can become very large. It is that cause, which can bring speed of transformation of NG directly to a magnitude exceeding by a million times the initial speed of the reaction (in absence of products of disintegration), and cause in this way fast thermal self-acceleration of process.

At the same time, we saw that at 20° the critical charge dimension for NG equals 150 m. If, however, the speed of reaction becomes a million times greater, then, repeating the same calculation, we will obtain a critical dimension 1000 times less, i.e., 15 cm. Moreover, it is necessary to consider that chemical self-acceleration also is an exothermic process and if it gives even a relatively small increase in temperature -- let us say, to 100° -- then the critical dimension will be lowered again to 6 cm.

Thus, the decisive factor in the triggering of explosion as a result of slow disintegration is the development of chemical self-acceleration of the process (due to accumulation of products of reaction).

Slow Disintegration of NG At Constant Temperature

Let us consider more specifically the main experimental regularities of the slow isothermal disintegration of NG and especially the self-acceleration of this process.

R. Robertson [6], studying the decomposition of liquid NG in a flow of inert gas which removes volatile products, showed that the speed of separation of oxides of nitrogen is constant, i.e., that decomposition in these conditions proceeds without acceleration. According to the value of the disintegration rate obtained by R. Robertson at various temperatures those kinetic characteristics were calculated (activation energy and pre-exponential multiplier) which we used in calculations by formula (1).

Investigations in the laboratory of the Moscow Chemico-Technological Institute (G. N. Bespalov, A. P. Glazkov, V. V. Gorbunov, N. D. Maurin, M. S. Plyasunov, B. S. Svetlov, V. P. Shelaputina [1], [2], [3], [4]), conducted by the manometric method, showed that in the initial stage the decomposition of NG proceeds without essential acceleration even if one does not divert the gasiform products of disintegration (Fig. 2). Moreover, in the initial stage the latter not only do not accelerate, but even delay the process; the greater the degree of filling of the vessel[1] with NG the lower the initial speed of decomposition (Fig. 3).

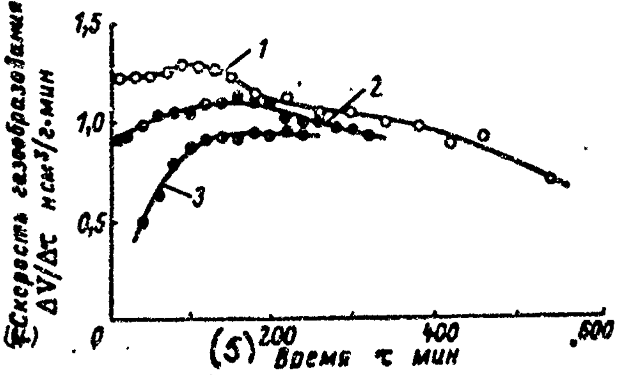

Fig. 2. Change in speed of gas formation in time in initial stages of disintegration of liquid NG at 140° and moderate degrees δ of filling of vessel. 1 - $\delta = 6.1 \cdot 10^{-4}$; 2 - $\delta = 12 \cdot 10^{-4}$; 3 - $\delta = 29 \cdot 10^{-4}$. Speed of gas formation is expressed by the number of cm^3 of gases (at 0° and 760 mm Hg) emitted in 1 minute in the conversion on 1 g of the substance; 4 - Speed of gas formation $\Delta V/\Delta\tau$ n $cm^3/g \cdot min$; 5 - Time τ, in min.

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[1] The degree δ of filling here and in the future is called the ratio of the volume of explosive to the volume of the vessel in which the experiment is conducted.

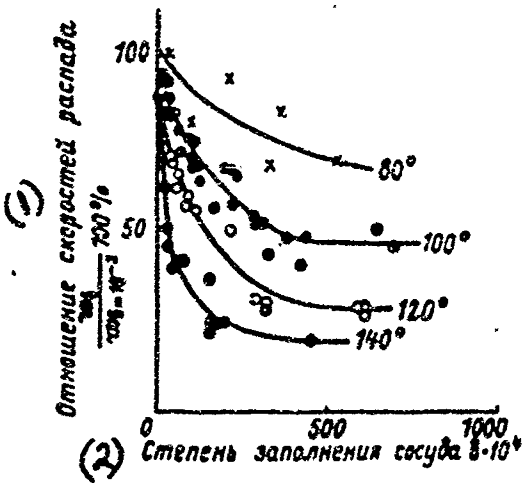

Fig. 3. Dependence of initial disintegration rate w of NG on degree of filling of vessel (δ) at experimental temperatures of 80 - 140°.
Along the axis of the ordinates there is placed the ratio of the disintegration rate at a given δ to the rate at $\delta = 10^{-3}$ in %.
1) Ratio of disintegration rates $\frac{w_\delta}{w_{\delta = 10^{3}}}$ 100%; 2) Degree of filling vessel, $\delta \cdot 10^4$.

However so the matter remains thus only as long as a certain critical pressure of the gasiform products of disintegration is not attained. After that a sharp acceleration of transformation begins (Fig. 4). Prior to achievement of the critical pressure, the disintegration rate grows proportionally to $\sim p^{1/2}$. Then this speed grows proportionally to the square of pressure (Fig. 5) which, according to the assumption of B. S. Svetlov, is connected with the influence of pressure on the concentration of the dimer (N_2O_4) in the gases and consequently, in the liquid.

Thus, one of the peculiarities of a self-accelerated reaction is its strong dependence on the concentration of gasiform products of disintegration, dissolved in liquid NG, which leads to a very fast growth in the speed of the process.

Another peculiarity of this reaction consists in the fact when self-acceleration of disintegration under the action of gasiform products was developed, the influence of temperature on its speed appeared to be very weak (Fig. 6).

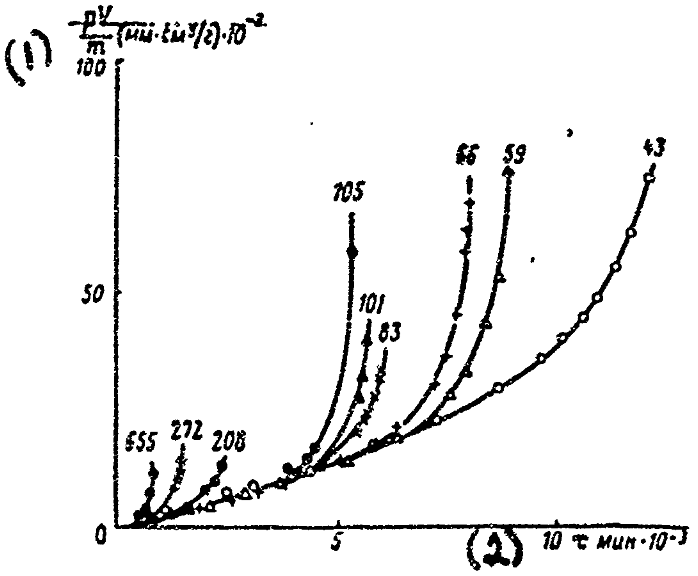

Fig. 4. Acceleration of disintegration of NG at 100° under the influence of gasiform products.
Numbers above curves - degree of filling of vessel, $\delta \cdot 10^4$. Along the axis of the ordinates there is placed the quantity of emitted gases, expressed in conditional units (pressure in mm Hg, multiplied by the volume of vessel in cm^3 and divided by the sample of explosive in g and by 1000).
1) p^V/m (mm · cm^3/g) · 10^{-3}; 2) τ, in min · 10^{-3}.

The combination of both these peculiarities leads to the fact that the manometric methodology, in its usual fulfillment (small δ), turns out to be unsuitable for investigation of the kinetics of the thermal disintegration of NG. Thus, since the substance in this case occupies only a very small part of the volume of the vessel, a large part of the gasiform products depart into the free volume of the latter and do not act on the transformation in the liquid phase. In practice, when we are concerned with a large volume of substance, i.e., with great thickness of its layer, the products of disintegration do not succeed, diffusing, to leave the explosive and are progressive accumulated in it.

The usual methodology creates difficulty also during determination of the dependence of reaction speed on temperature: an increase in the latter decreases the solubility of the gasiform disintegration products in the liquid phase and this can lower the growth in speed and even prevent acceleration of the process, as was observed by B. S. Svetlov in the known condition of experiment. On the other hand, in industrial volumes lowering of the solubility with temperature is not certain to succeed, by the above-mentioned causes, to decrease the concentration of gasiform products in liquid NG.

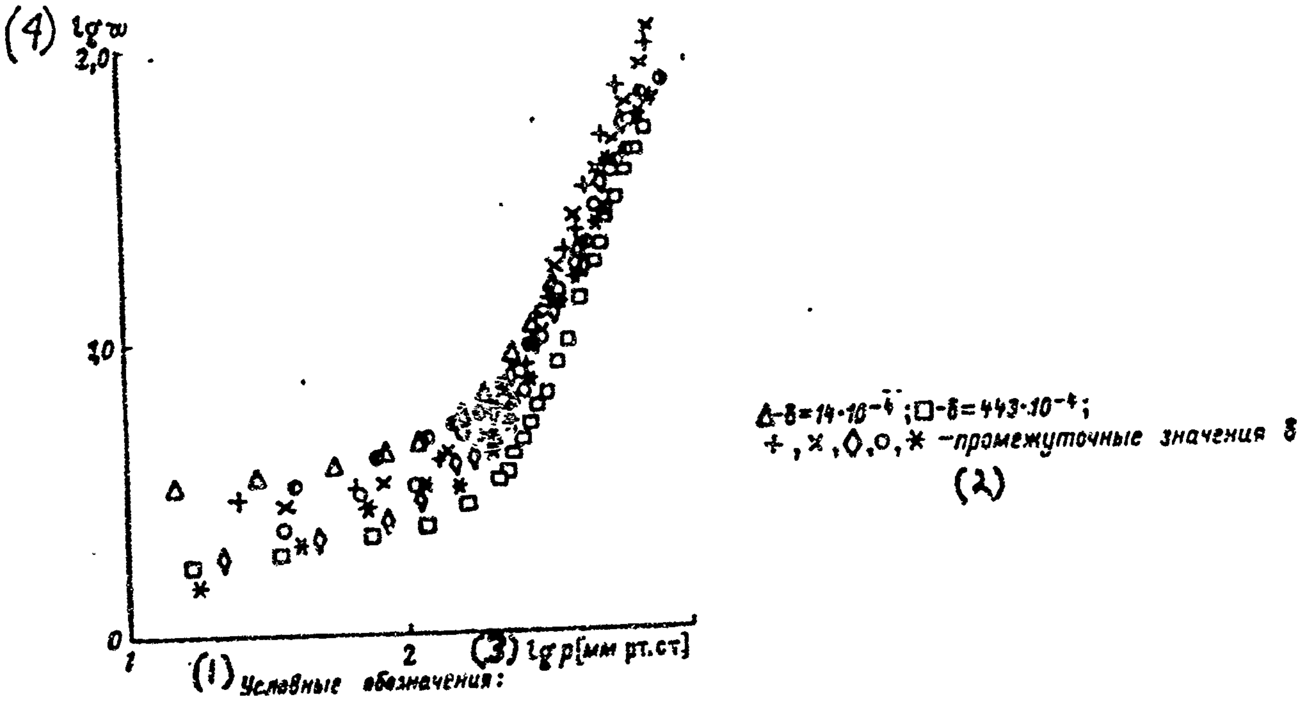

Fig. 5. Dependence of specific speed of gas formation (w) on pressure of gasiform products of NG disintegration at 100° at various degrees of filling of the vessel δ.
Speed is expressed in conditional units. 1) Conditional designations; 2) Intermediate values of δ : 3) log p [mm Hg]; 4) log w.

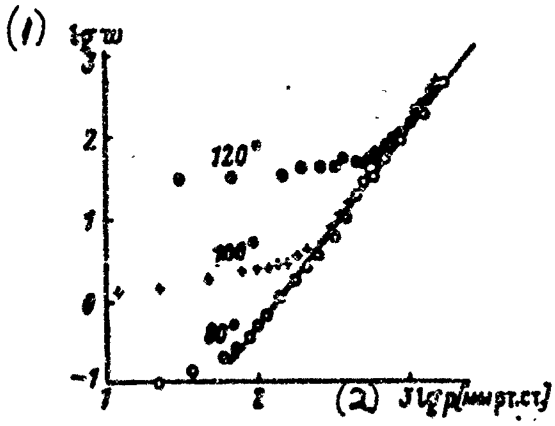

Fig. 6. Dependence of specific speed of gas formation (w) on pressure of products of NG disintegration at various temperatures. 1) log w; 2) log p [mm Hg]
Disintegration rate is expressed in conditional units.

In order to approach real conditions, we modified the methodology of laboratory experiments filling of vessel by nitroglycerine almost completely; this assured practically full preservation in the liquid phase of the gasiform products of transformation. In these conditions sharp acceleration of disintegration at 100° sets in already after 9 - 10 hr., at 80° after 73 - 93 hr., and at 60° after

550 hr. These data make it possible to calculate by extrapolation the corresponding values of the time of onset of acceleration at lower temperatures. For 30° we will obtain 3.2 yr., for 20° - 17 yr. The values obtained for the time of beginning of sharp acceleration of NG disintegration although great, but they are incomparably less than in case of decomposition with removal of products of disintegration, when this time even for certain small fractions of the explosive, say 2%, constitutes 4800 and 56,500 years at 30° and 20°, respectively.

Influence of Certain Impurities on the Slow Disintegration of NG

Above we spoke about the disintegration of pure NG, free from impurities. Of the biggest practical interest impurities which usually can be found in NG water and acid present.

Water is soluble in NG. By our determination (V. V. Gorbynov; see p. 219 in this collection) water is dissolved in NG at 20° by 0.25%, at 30° - 0.31%, and at 60° - 0.49%.

However, contents of H_2O can be larger, since it can be in NG, not only in the dissolved, but also the suspended form. For this reason technical NG is usually cloudy.

Water shows a significant and specific influence on the slow transformation of NG. According to the experiment of G. N Bespalov (see p. 131 in this collection), at elevated temperatures (80 - 100°) and small contents of H_2O, the curve $p=f(\tau)$ has the same character as in the absence of water (Fig. 7), but the time to beginning of acceleration of disintegration is less in the first.

At large contents of water the character of the curve changes considerably: for a long time pressure remains constant and practically equal to the vapor tension of water over NG; then a sharp fall sets in, caused by the transition of water to the liquid phase. After this fall there begins a starts more or less fast growth of pressure. The general time to the onset of sharp acceleration of disintegration in presence of water is strongly reduced as compared with time for the anhydrous product. Thus, at 100° and $\delta = 0.03$ the time to sharp acceleration of decomposition of anhydrous NG constituted nearly 2400 min, but at a water-vapor pressure equal to 400 - 500 mm, it was reduced to 150 min. At maximum δ (near 1) at 100 and 60° in the presence of 0.2% H_2O the indicated time was 2½ times less than for anhydrous NG.

If one were to add to NG still more water, the character of the curve $p=f(\tau)$ changes anew. For a long time a very slow and weak fall of pressure is observed and only on the expiration of a significant larger time than for even anhydrous NG sharp acceleration of the process is observed.

Thus, water in small quantities accelerates the transformation of NG, the more strongly the bigger its addition. In great quantities it delays the beginning of acceleration of disintegration of nitroglycerine.

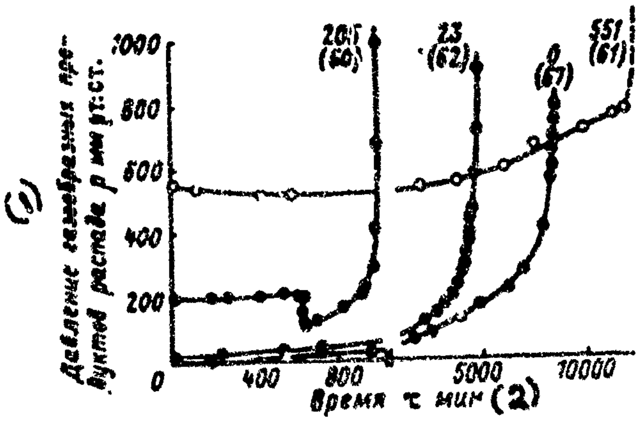

Fig. 7. Influence of water on disintegration of NG at 100° and different degrees of filling of vessel δ.
Numbers by the curves - pressure of water vapor over NG in mm of mercury and (in parentheses) $\delta \cdot 10^4$.
1) Pressure of gasiform products of disintegration (p), mm Hg; 2) Time τ, min.

Accelerating influence on the disintegration of NC is shown also by acids, in particular by nitric acid. Starting corresponding investigations, we, proceeding from generally accepted assumptions, expected that very small contents of acid would very strongly accelerate the decomposition of nitroglycerine. Experiments did not confirm this expectation. Thus, in case of addition to NG of HNO_3 in a quantity of 0.3% by weight, the time to onset of acceleration of the reaction was reduced in all by twice as compared with neutral product (see curve 4, Fig. 8).

Moreover, a comparison of equal(by pressure of their vapor over NG) quantities of nitric acid and water (curves 2 and 3, Fig. 8) showed that at 100° the acid accelerates the disintegration of NG approximately the same as water; however, their joint presence at a giver pressure did not reduce the time to beginning of acceleration of the process. Finally, experiments in the presence of large quantities of water (Fig. 9) showed that 0.02% nitric acid by weight of NG has little effect on the course of disintegration. Thus, for example, at near contents of water the induction period in presence of acid was lowered only from 70 (in the absence of acid) to 68 min. A strong influence of nitric acid in the presence of water is developed only at relatively large (~1.5%) contents of acid in NG (Fig. 10).

All these observations are explained by the assumption that fast transformation, setting in at the stage of acceleration, is caused by hydrolysis of NG, which is strongly accelerated by acids in a definite interval of concentration, and the oxidation-reduction reactions accompanying hydrolysis, occurring between its products with the possible participation of the initial nitro ester. If one

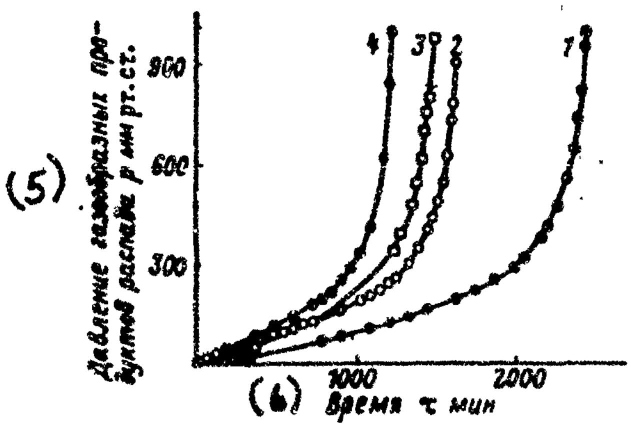

Fig. 8. Influence of moderate (0.3%) quantities HNO_2 on disintegration NG at 100°.
1—NG, neutral anhydrous, $\delta = 0.0329$; 2—$NG + H_2O + HNO_3$, $p = 14$, $\delta = 0.0281$; 3—$NG + H_2O$, $p = 14$, $\delta = 0.0271$; 4—$NG + HNO_3$, $p = 13$, $\delta = 0.0346$; p = general equilibrium pressure at the beginning of the experiment in mm Hg; δ — [defined above]; 5—Pressure of gasiform products of disintegration (p), mm Hg; 6—Time τ, min.

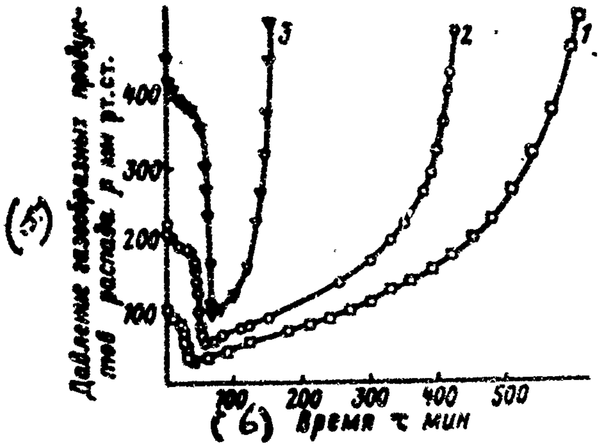

Fig. 9. Influence of small (0.02%) quantities HNO_3 on disintegration of NG at 100° in presence of water.
1--NG + H_2O + 0.023% (by wt) HNO_3, p = 92, δ = 0.0363; 2--NG + H_2O + 0.017% (by wt) HNO_3, p = 196, δ = 0.0287; 3--NG + H_2O + 0.019% (by wt) HNO_3, p = 385, δ -- 0.0317; p = same as Fig. 8; δ --[defined above]; 5,6 --same as Fig. 8.

were to eliminate the effect of acids -- for example, with the help of soda located in the vessel joined to the ampule with NG -- then as a result of the neutralization of the acid vapors, the acceleration of transformation does not set in either in presence of water or in its absence.

Water introduced in neutral NG acts relatively slowly as long as acid is not accumulated in the product as a result of "anhydrous" reaction or hydrolysis; if water is not introduced, the accumulation of acids and water (as a result of oxidizing reactions) proceeds still slower. Nitric acid in itself acts slowly, in particular because time is required for the formation of water. The most active is water in the presence of acid; this acid need not be nitric.

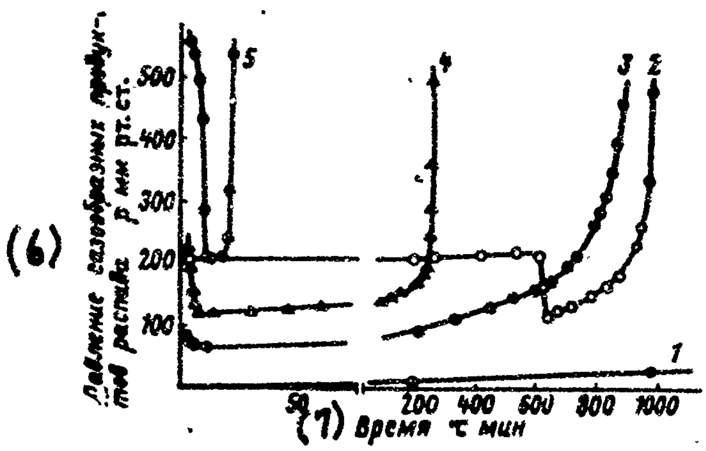

Fig. 10. Influence of significant (1.5%) quantities of nitric acid on disintegration NG at 100° in presence of water.
1--NG, neutral anhydrous; δ - 0.0061; 2--NG + H_2O, p = 205, δ = 0.0060; /3--NG + HNO_3, p = 82.5, δ = 0.0062; 4--NG + H_2O + HNO_3, p = 222, δ = 0.0070; 5--NG + H_2O + HNO_3, p = 560, δ = 0.0068; p = same as Fig. 8; δ -- [defined above]; 6--Pressure of gasiform products of disintegration (p), mm Hg; 7--Time τ, min.

It is necessary to add that we studied chiefly the influence of mixtures of water with nitric acid. It should not, however, be considered that this combination is the most effective stimulator of acceleration of transformation of NG.

Experiments of V. P. Shelaputina showed that water combined in definite relationships with oxide and nitrogen peroxide serves as a very energetic accelerator. Thus in one experiment at 80° (Fig. 11), in which the equilibrium pressure of water vapor constituted about 100 mm Hg, acceleration of the disintegration of NG set in only after 2000 min; with the simultaneous presence of water, NO, and NO_2 a sharp growth of speed of gas formation was observed already after 50 min after the beginning of the experiment (see curve 2, Fig. 11).

Apparently, in experiments with water the direct product of hydrolysis is nitric acid. Interacting with dinitrate and trinitrate formed during hydrolysis, it will form nitrogen dioxide and nitrogen peroxide, whose oxidizing action in the presence of water is significant greater, than that of nitric acid. The reactions of interaction of nitric acid and nitrates proceed relatively slowly, by which is determined the significant interval of time between the moment of pressure drop in experiments with water and the onset of its sharp growth.

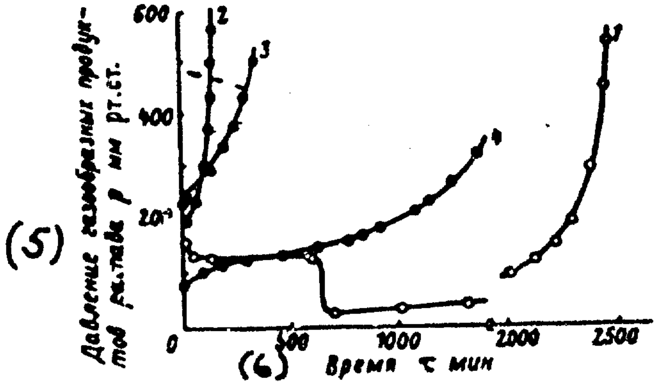

Fig. 11. Influence of oxides of nitrogen on disintegration of NG at 80° in presence of water.
1--NG + H_2O, p_{H_2O} = 284, δ = 0,0304; 2--NG + H_2O + NO + NO_2, p_{H_2O} = 246, p_{NO} = 32, p_{NO_2} = 100, δ = 0,0312; 3--NG + H_2O + NO + NO_2, p_{H_2O} = 100, p_{NO} = 130, p_{NO_2} = 110, δ = 0,0302; 4--NG + H_2O + NO + NO_2, p_{H_2O} = 31, p_{NO} = 30, p_{NO_2} = 37 = δ 0,0309; p - calculated pressure of vapors and gases introduced into the vessel at the beginning of the experiment (without calculation of their possible interaction and dissolution) in mm Hg; δ - degree of filling of vessel with nitroglycerine; 5--Pressure of gasiform products of disintegration (p), mm Hg; 6--Time τ, min.

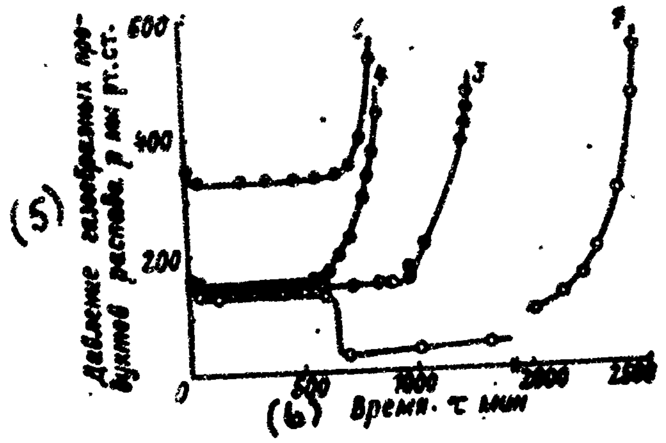

Fig. 12. Influence of oxides of nitrogen on disintegration NG at 80° in presence of water.
1-NG+H2O, p_{H_2O} =284, δ = 0,0304; 2—NG + H_2O + NO, p_{H_2O} = 272, p_{NO} = 214, = δ 0,0328; 3—NG + H_2O + NO, p_{H_2O} = 238, p_{NO} = 50, δ = 0,0329; 4—NG + H_2O + NO, p_{H_2O} = 230, p_{NO} = 50, δ = 0,0294; p, δ , 5, 6—same as Fig. 11.

If one introduces the oxides of nitrogen immediately then oxidation of nitrates starts quickly.

Additional evidence in favor of the described sequence of reaction is contained in the results of experiments on the decomposition of NG in the presence of water and oxides of nitrogen (Fig. 12). Induction period in these experiments preserved its character (constancy of pressure) and duration. However, on the one hand, that pressure drop upon completion of the induction period, which is observed in the presence of water, but the absence of oxides of nitrogen, is absent in this case, and on the other hand - acceleration of gas formation after induction period is developed much more sharply and faster. The absence of the pressure drop may be connected with the fact that nitric acid with oxide of nitrogen will form nitrous acid, whose solubility in NG is supposedly less than that of nitric, but whose oxidizing action is greater. Correspondingly, against the background of fast growth of pressure as a result of oxidation, it is possible that a small pressure drop at the expense of dissolution remains unnoticed.

Slow Disintegration of NG At Low Temperatures

The experiments described above were conducted at relatively high (80° and higher)temperatures.

Experiments at lower (40 - 80°) temperatures (B. S. Svetlov and V. V. Gorbunov) take a very long time and therefore were few. They showed that regularities determined at elevated temperatures are qualitatively correct also for significantly lower temperatures, but have certain quantitative distinctions.

Thus at 100° and a high degree of filling of vessel, in the presence of 0.2% by weight of nitric acid sharp acceleration sets in 1.7 times faster than for anhydrous neutral NG; water acts more strongly than nitric acid and at the same content lowers the indicated time by 2.5 times (Fig. 13).

At still lower temperatures (60 and 40°) acid and water also reduce the induction period, but acid acts more strongly than water[1]; also, this distinction increases during the transition from 60 to 40°. Besides, at low temperatures the influence of additions to NG is greater in the sense of the relative decrease of the induction period. This not surprising. With a lowering of the temperature, the speed of reactions of decomposition, forming acid and water, decreases; correspondingly the influence of this source of accelerating impurities is lowered and the role of accelerators introduced from without is relatively increased.

It is necessary to indicate also that in all these experiments we have spoken of contents of additions on acid character which although small, are still incomparably larger than those insignificant quantities which are registered by

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[1] It is necessary however to keep in mind that for water, in contrast to nitric acid, there is a certain optimum content at which the induction period is smallest. The optimum content was established only for 100°; at low temperatures no corresponding experiments were conducted.

the standard method of determination of NG stability - the iodised starch test.

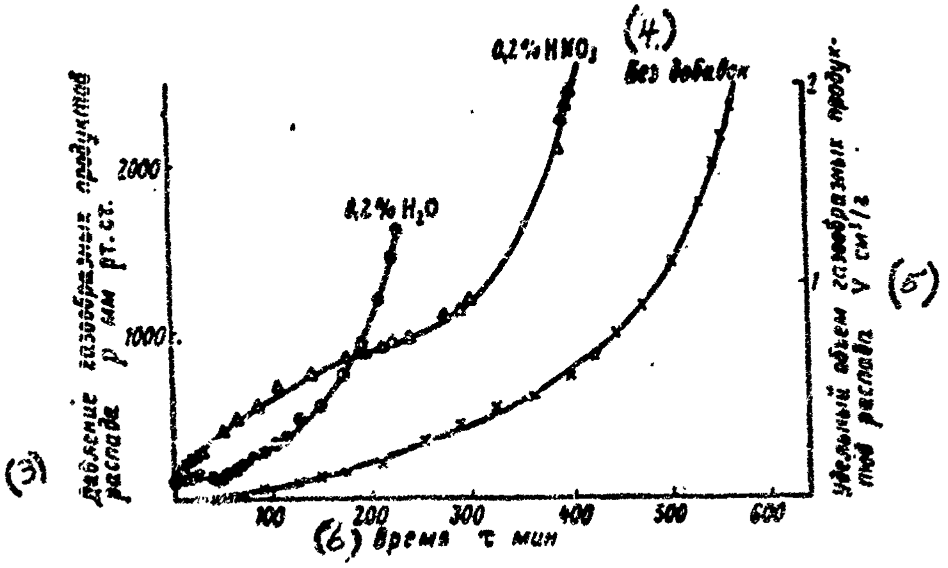

Fig. 13. Influence of water and nitric acid on disintegration of NG at 100° and high degree of filling of vessel ($\delta \approx 1$).
3) Pressure of gasiform products of disintegration (p), mm Hg; 4) Without additions; 5) Specific volume of gasiform products of disintegration (V), cm^3/g; 6) Time τ, min.

Peculiarities of Development of NG Decomposition To Flash

From the considered experimental data it follows that NG is susceptible to two processes of transformation; one is realized at relatively high temperatures and is characterized by strong dependence of speed of transformation on temperature. The speed of the second process strongly depends on the concentration of products of NG disintegration, (oxides of nitrogen and water) and weakly on temperature. Therefore, at low temperatures, when the constant of the speed of the first process insignificant, the actual disintegration rate of NG can be determined only by the second process. This speed, however, in the beginning of the process is very small, provided that a sufficient amount of acid and a little water are not introduced into the NG. During the decomposition of initially neutrally and anhydrous NG there will be formed nitrogen dioxide and as a product of the oxidation of water; if the NG contains water, the formation of nitric acid and then of oxides of nitrogen is significantly accelerated.

One would think that at low initial temperatures just the second process and should bring NG to thermal triggering of flash. However this, apparently, is not so, because the speed of reactions of the second process grow only very weakly with temperature. Correspondingly, the speed of the transformation determined by them can attain values at which the expression of Frank-Kamenetskiy (1) becomes equal to the critical only at relatively high temperature. Calculations carried out according to the kinetic parameters (E and B) of the second process, established for the stage of sharp acceleration, give at r = 1 mm a critical value of temperature of ~600° (580°). As we have seen, analogous calculations for the first process—a reaction proceeding in the absence of products of disintegration—gave a significantly smaller temperature (163°). Therefore during development of acceleration of disintegration by reaction products and during the heat up accompanying earlier, there will be attained the critical speed for that process; it will proceed ever faster and faster and, at last, will attain the critical speed of transformation, independent of the products of nitro ester decomposition.

Here, however, it is necessary to make one reservation: the speed of reactions in the presence of gasiform products of disintegration strongly depends on their concentration: the above-cited calculation data refer to that case when the pressure of these products over NG is small(2 technical atmospheres), since during the development of the process in ordinary conditions it is difficult to imagine the possibility of achievement of higher pressures. However, if such conditions exist then the critical temperature is approached for both reactions. If we allow that the dependence on pressure of the speed of the self-accelerated process fixed by experiment for the interval of temperatures of 80 - 120° and also its independence from temperature are secured at more higher values of the latter, then at 163° the speed of the process, proceeding under the influence of products of disintegration, will be at 9 technical atmospheres equal to its speed in their absence.

If a strong increase in pressure cannot occur, then the development of reaction to flash takes a unique three-stage character. In the first stage, either as a result of the first process (if the temperature is not very low), or owing to hydrolysis of neutral or acid NG, there will be formed products of disintegration. This stipulates the development of the second process. On following stage this process as a result of accumulation of products of disintegration, is self-accelerated to such a degree that a significant increase in temperature occurs. In the third stage the first process has predominant signifigance; its thermal acceleration brings the NG to flash. The time to onset of flash is determined by the second process, and its critical conditions by the first. Of course, both processes proceed not autonomously but jointly, and they are interconnected, so that what has been said represents the naturally known schematization of the phenomenon. The higher the initial temperature and the more favorably the conditions for removal of gasiform products from liquid or binding them, the greater is the expressed role of first process and vice versa.

The above refers to anhydrous NG. In the presence of moisture goes a hydrolytic process proceeds parallel with the first one; its speed greater than that of the first. The remaining kinetic characteristics of this process have been little studied. In other respects decomposition to flash in this case is developed analogously to that of anhydrous NG.

Conclusions

The disintegration of NG, proceeding very slowly and without acceleration with removal or binding of its products (at low temperatures) and without acceleration, can be strongly accelerated if the products of this disintegration are retained. The onset of acceleration of decomposition occurs much faster if the NG contains impurities - water (in definite limits) and acids or oxides of nitrogen. A peculiarity of reactions self-acceleration is their strong dependence speed on concentration of products of disintegration or of impurities and weak dependence on temperature. Due to this, if a high concentration of accelerating substances is attained, disintegration can lead to thermal triggering of flash even at very low temperatures and relatively small dimensions of charge.

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K. K. Andreyev, and B. I. Kaydymov

18. Thermal Disintegration of PETN

The introduction into technology of pentaerythritė tetranitrate (PETN) demanded a thorough study of its properties, in particular chemical stability, the more so, as PETN belongs to the number of esters of nitric acids, which, as was known, in general, are greatly inferior in this respect to nitro compounds of the aromatic series and even nitramines.

Chemical stability of PETN and mixtures in its base, the method of its determination and the effect on it of certain impurities were studied in a number of works. Already the first investigations had shown that the chemical stability of PETN was considerably more, than other nitro esters close to it according to the number of nitrate groups in the carbon atom, and consequently, also according to the energy of the explosive nitroglycerine, nitroglycol and even nitrocellulose significantly exceeding their stability. Thus, by Abel's test at 75°, which dynamite nitroglycerine sustains usually for 15 minutes, PETN does not react at 80° even for 50 minutes. This circumstance is usually connected with the high symmetry of the PETN molecule by comparison with nitroglycerine, having linear structure [16],[17]. Thus, Stettbacher, and later other investigators, have considered that location of a 4-x mathoxynitro group around the central carbon atom in PETN determines its high chemical stability. The same opinion is expressed by L. Avogadro, who considers that PETN thanks to its symmetric structure to be the stablest of nitro esters.

One of the most thorough investigations into this question was published by Picardo [14]. He exposed 2 samples of PETN to 100 and 105° for 450 days and after definite time intervals established the change of their properties. After each 15 days a test was made at 120° with methylviolet paper and a loss in weight was determined. With an interval of 60 days the investigator made several tests; Taliani's test at 125°, Bergman - Young's at 132° and Anjeli's and also determined the contents of nitrogen according to Lunge and the melting point.

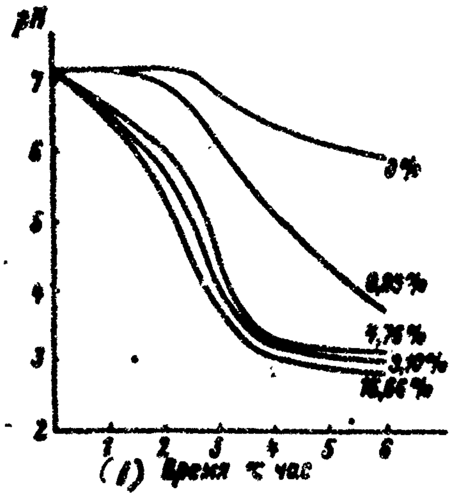


Fig. 1. Change of pH during decomposition of PETN in the presence of different quantities of trotyl (according to Urbanski and others) at 120°. Numbers by curves-contents of trotyl in mixture in % weight.

1) Time τ hour.

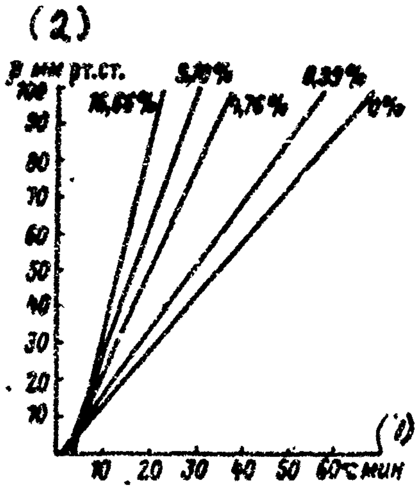


Fig. 2. Change of pressure during decomposition of PETN presence of different quantities of trotyl (according to Urbanski and others). Numbers by curves-contents of trotyl in mixture in % weight.

1)τ Minutes; 2) p mm of mercury.

The last determination was conducted also with crystals, condensed as a result of sublimation on the walls of the vessel.

Results of tests showed that stability not only does not decrease time, but is noticeably increased. At 105° this process goes faster, than at 100°. Loss in weight increases approximately proportional to time. Contents of nitrogen somewhat increase, just as melting point (140.3 - 141.2° in beginning of experiment and 141.3 - 142.0° after 450-day heating at 105°). The sublimate has a higher melting point, that the initial PETN and the narrowest range of melting (142.0 - 142.2°).

From these data it follows that long heating leads to the sublimation not only of PETN, but also of impurities, contained in the original product, and they either are sublimated without being decomposed, or being decomposed, they will form highly volatile and fully removed products. In general, these experiments show that even very long heating of PETN in an opened vessel at 105° does not lead to noticeable decomposition of explosive, but, on the contrary, increases its cleanness and stability.

Urbanski, Kwiatowski and Miladowski [19] studied the effect of nitro derivatives of aromatic series on the chemical stability of certain nitro esters, in particular, PETN. Investigation was carried out by means of determining pH mixtures, heated at 100 - 120° and by Taliani's method at 134.5°, modified by Guzhon. Graphs in Fig. 1 and 2 illustrate the results of the experiments. Nitro compounds lower the stability of PETN, and in this way act more strongly at given percentage (by weight) of mononitro compound, then diand trinitro compound. This effect becomes stronger in the first hours of heating. Derivative benzenes act somewhat more strongly, than derivative toluene. It is interesting that nitro derivatives do not accelerate the decomposition of nitromannite.

Analogous results were received by Tonegutti [18], who determined the stability of PETN and its mixtures with trotyl by Teliani's test at 120, 125 and 135°. Some of his results are presented in table 1.

Table 1

Stability of PETN and Its Mixtures With
Certain Explosives by Teliani's Test

(2) Температура опытов °C	(1) Время достижения давления 300 мм рт. ст. в час					
	(3) Тэн	(4) Тэн с 30% ТНТ	(5) Тэн с 50% ТНТ	(6) Тэн с 10% пикриновой кислоты	(7) Тэн с 20% нитроглицерина	(8) Нитроклетчатка
120	20,50	5,08	5,16	2,33	2,75	5,08
125	11,25	2,08	—	—	—	3,66
130	7,00	1,00	0,92	—	—	1,70

1) Time to achieve pressure of 300 mm of mercury in hours; 2) Temperature of Experiments °C; 3) PETN; 4) PETN with 30% TNT; 5) PETN with 50% TNT; 6) PETN with 10% picric acid; 7) PETN with 20% nitroglycerine; 8) Nitrocellulose.

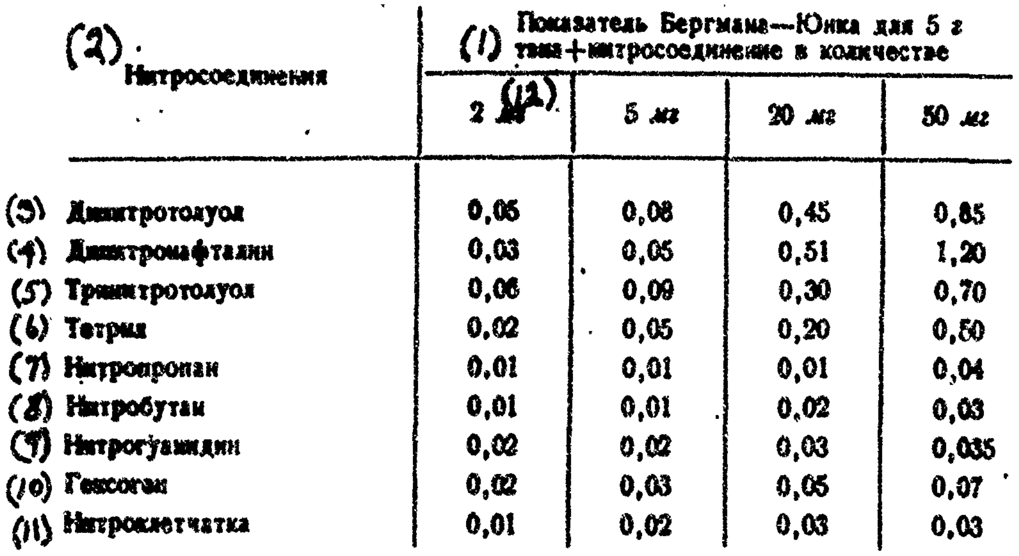
From other observations of Tonegutti one should note that stability of tetryl at 120 - 125° is 3 - 4 times more than PETN, while at 130° it is less by a factor of 2 than for PETN. In the opinion of this investigator, this connected with the fact that in the latter case temperature of the experiment is too close to critical temperature of decomposition.

Conclusions of Urbanski and Tonegutti are confirmed also by Bourjol's experiment [9] (Table. 2), which determined by the Bergman-Young test the effect on stability of PETN additions of different aromatic and aliphatic nitro compounds. All the aromatic nitro compounds, to the greatest degree dinitronaphthalene, lower the stability of PETN. The action of aliphatic nitro compounds is incomparably less. Bourjol concludes: "Aromatic nitro compounds act on PETN, decomposing it with the formation of oxides of nitrogen. The mechanism of this action is apparently not known".

Urbanski and Miladowski [20] in the later work studied by the pH method the effect on stability of PETN at 132° of different nonexplosive substances in a quantity of 3 - 5% weight (ethyl and propyl alcohol, ethyl ether, ethyl acetate, isoamyl acetate, acetone, acetophenone, water) and in a quantity of 0.1 - 1.0% weight (diphenylamine and centralite) and showed that all of them to a greater or lesser degree lower its stability.

Table 2

Stability of PETN and its Mixtures with Certain Explosives by Bergman-Young Test



(2) Нитросоединения	(1) Показатель Бергмана—Юнка для 5 г тэна+нитросоединение в количестве			
	2 мг (12)	5 мг	20 мг	50 мг
(3) Динитротолуол	0,05	0,08	0,45	0,85
(4) Динитронафталин	0,03	0,05	0,51	1,20
(5) Тринитротолуол	0,06	0,09	0,30	0,70
(6) Тетрил	0,02	0,05	0,20	0,50
(7) Нитропропан	0,01	0,01	0,01	0,04
(8) Нитробутан	0,01	0,01	0,02	0,03
(9) Нитрогуанидин	0,02	0,02	0,03	0,035
(10) Гексоген	0,02	0,03	0,05	0,07
(11) Нитроклетчатка	0,01	0,02	0,03	0,03

1) Bergman-Young Index for 5 g of PETN nitro compound in quantity; 2) Nitro compounds; 3) Dinitrotoluene; 4) Dinitronaphthalene; 5) Trinitrotoluene; 6) Tetryl; 7) Nitropropane; 8) Nitrobutane; 9) Nitroguanidine; 10) Hexogen; 11) Nitrocellulose; 12) mg.

These substances have a reverse effect on nitrocellulose: they noticeably increase its stability. On the basis of this, different authors have concluded that an "essential difference" exists between chemical properties of nitrocellulose and PETN, a difference, which, they consider, is caused by the completely different structure of both nitro esters, and namely, by the high-molecular chainannular structure of nitrate of cellulose and the branched structure of PETN with its central atom of carbon.

To similar conclusions have arrived other investigators, studying the effect on nitro compounds on decomposition of PETN. Thus, Desseigne [10] by heating mixtures of PETN with trotyl in closed test-tubes at 90° established that with significant contents of trotyl the rate and acceleration of gas formation strongly increase (fig. 3). This acceleration the author connects with the formation of oxides of nitrogen - gas phase takes clear color.

A similar picture is also observed during decomposition in loosely closed vessels at 120°, when the pressure could not be increased, but gasiform products of disintegration did not escape so easily, as during experiment in opened vessels. At 110° the effect of trotyl is developed even more abruptly and with less of its content. In analogous conditions the presence of trotyl appeared to have an incomparably smaller influence on the decomposition of hexogen.

Investigations on the stability of PETN were published also by Aubertein. He determined the rate of gas formation during decomposition of PETN in a vacuum at 120° [5], by the method, applied in England for the determination of the stability of PETN, according to instruction of the standard. Rate of gas formation does not depend on dimensions of crystals. All samples showed one and the same rate of decomposition before and after thorough crushing in an agate mortar, both the case of PETN, obtained by recrystallization from the usual purified acetone, and also for PETN, precipitated from acetonic solution by water.

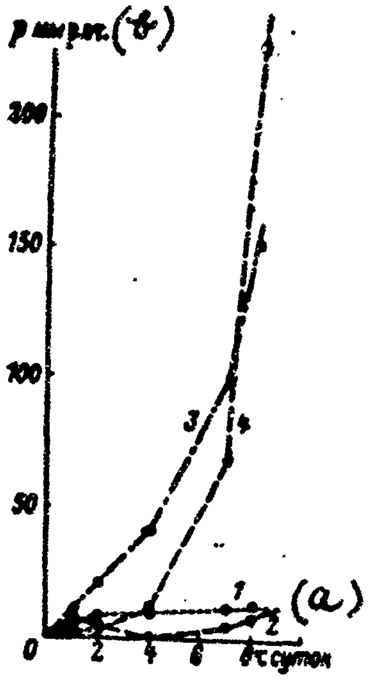


Fig. 3. Change of pressure during decomposition of PETN in presence of trotyl at 90° (by Desseigne). 1 - pure PETN, 2 - mixture PETN - trotyl (75 : 25), 3 - mixture PETN - trotyl (50 : 50), 4 - mixture PETN - trotyl (25 : 75).

a) τ 24 hour periods; b) P mm of mercury.

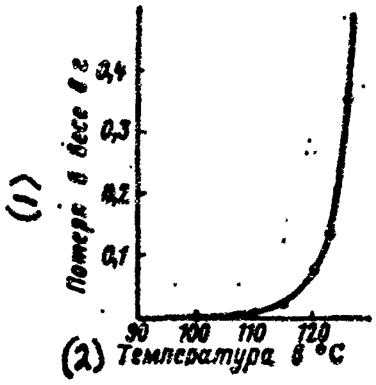


Fig. 4. Change in rate of hydrolysis of PETN, characterized by loss in weight at different temperatures (by Aubertein).

1) Loss in weight in g; 2) Temperature in °C.

Such PETN, especially if precipitation is produced from acetonechloroform solution, shows a significantly lowered stability that is connected with the chemical effect of radicals of solvent (hydrolytic action of water, formation of hydrochloric acid, impurity of acetone). Nitric acid accelerates disintegration, although its action in the absence of water is weaker than hydrolytic action of water. This last action in many cases turns out to be more essential, than the effect of other impurities, if their quantity does not exceed a certain limit.

The other work of Aubertein [6] considers the effect of including solvents or precipitators, which can strongly lower indices of stability by Bergman-Young (test, applied for PETN in France) as a result of transition of disintegration of the tested explosive substances from thermal to hydrolytic. Thorough crushing of crystals, ensuring during subsequent drying the removal of volatile impurities (water, acetone) leads to a sharp increase of stability index. Separate experiments [7] indicated that the rate of hydrolysis of PETN is great and it grows especially fast with temperatures above 120° (fig. 4). In one experiment at 130° hydrolysis lead to explosion.

The weak side of Aubertein's works is the conduct of experiments just below the melting point of PETN. The effect of impurities can be twofold; chemical or physical. Conducting comparative experiments with liquid substance, it would have been possible to exclude the effect of the physical factor. Inasmuch as this was not done, it is difficult to determine, what part of the accelerating effect of radicals of acetone, water and chloroform one should relate to transference by them of part of the solid PETN into liquid state.

One of the last works based on the explanation of the effect of impurities on the stability of PETN is the investigation of L. Avogadro [8]. He expanded the studied range of temperature downward, determined the effect of not only trotyl, but also certain substances (diethyleneglycoldinitrate, pentaerythritolacetate), which were not studied by his predecessors, and also attempted to understand the cause of the observed lowering of stability of PETN. By Anjeli's tests at 120° and Telieni's at 125° and several lower temperatures(below 90°) mixtures of PETN with all three substances added to it gave a more or less strong decrease of stability. These results are confirmed also by potentiometric puncture. If, however, this test is conducted at low temperature (75°) below eutectic point, then stability after 60 day heating turns out to be for mixture with trotyl (50 : 50) even somewhat more, than for PETN (change pH from 6.76 to 5.99 in first case and from 6.80 to 5.80 in second). The results obtained by L. Avogadro compares with the solubility of PETN in mixed substances; it constitutes at 90 and 100° respectively for trotyl 25 and 66 parts in 100 parts of solvent, for pentaerythritolacetate 30 and 100 parts and for diethyleneglycoldinitrate 22 and 66 parts. The weak effect of impurities of these substances on the stability of hexogen Avogadro connects with its relatively low solubility in them. This also explains the decrease in the case of PETN of the effect of impurities with a lowering of temperature and the sharp increase of stability of mixtures below 75°. Hence L. Avogadro correctly concludes that if the mixtures do not contain a liquid phase, then lowering of stability is absent.

From the survey of works presented published on this question it is clear that investigators are gradually approaching the correct understanding of the mechanism and significance of the effect of nitro compounds and other impurities on the stability of PETN. The slowness of this approach has a singular cause. All the above mentioned investigators forgot two works [11], [13], published in 1920 and 1921, in which in an example of tetryl it was shown that the decomposition rate in melt or solution is much greater than in solid state. This observation is fully applicable to the case of PETN, as was shown in 1939 - 1940 in an unpublished work of K. P. Maslov (Moscow Chemico-Technological Institute in the name of Mendeleyev). In this work, delivered to explain the results of the investigation of Urbanski, Kwiatkowski and Miladowski, the stability of PETN was compared by Taliani's method with the stability of its mixtures with trotyl[1]. It was established that at temperatures below 140° the stability of mixtures is significantly lower than the stability of PETN, while above this temperature (experiments were conducted at 145°) difference in stability is absent. It was established also that at least in the initial stage the disin-

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[1] In this work were experiments based on the study of the stabilizing effect of nitro compounds on decomposition of nitrocellulose established by Urbanski and collaborators. The initial position was the assumption that disintegration of nitrocellulose starts by surface reaction; by covering the surface of pyroxylin with liquid it is retarded just as for example, the disintegration of azide of calcium is retarded by paraffin. The experiment showed that paraffin noticeably delays decomposition of nitrocellulose; however, considering the detected effect of many factors during disintegration, the authors do not consider their assumption definitely confirmed by these experiments.

tegration rate of PETN in trotyl solution does not depend on concentration, i. e. that disintegration is a reaction of the first order. From the independence of disintegration rate from impurity of nitro compounds at a temperature above the melting point of PETN (141°) the conclusion was made that "decomposition rate of pure PETN does not change during the addition of nitro compounds, which do not form chemical compounds with it". and further "Literary indications on this question (works of Urbanski, Kwiatkowski, Miladowski) do not correspond to reality, due to the omission of a way of distinguishing states of aggregations during the conduct of comparative experiments".

The work considered in the present article had as a goal a plan of general investigation of thermal decomposition of nitro ester to study thermal disintegration of PETN during the different conditions of its course, and also the effect of certain impurities on it in order to try to give an explanation to earlier established peculiarities of given explosive substances[1].

Experimental Part

Method of Work

In this work the manometric method was applied in its version [1], which has a number of essential advantages over methods, applied earlier: expulsion of distillation products to the cold parts of the instrument, and also the effect on the disintegration process of air, vapors of sealing and manometric liquids. Besides, the substance and the products of its decomposition are in contact only with glass. Decomposition of the tested substance started in a vacuum or in an atmosphere of those gases or vapors, whose effect was studied.

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[1] For a more detailed description of method and results of work, see [4].

The investigated PETN was thoroughly freed from volatile impurities, which could affect its disintegration. For this the system was pumped to pressure no higher than 10^{-3} mm of mercury during simultaneous heating of reaction vessel by water with a temperature of 80 - 100°. During the preparation of the experiment on decomposition of mixtures of PETN+TNT the evacuation of volatile impurities was produced in two stages. Initially into the reaction vessel was introduced only TNT, lateral branch of the vessel was closed by rubber with clamp, and trotyl was pumped in melted state at a temperature of 80 - 90°. Periodic cooling and heating of trotyl to a significant degree facilitates its elimination of volatile impurities, since the latter very violently are liberated in the moment of crystallization. After full separation of volatile impurities trotyl was cooled and a weighed amount of PETN was introduced, after which the lateral branch of the reaction vessel was soldered and evacuation was carried out just as with TNT alone.

During the investigation was used PETN of factory production, twice recrystallized from pure acetone by cooling, with a melting point of 141.3° and with dimensions of crystals less than 1 mm.

For experiments on decomposition of PETN in trotyl solution TNT was used with a melting point of 80.6°.

Results

Disintegration of PETN in Melt

In order to make it possible to compare PETN with respect to character and disintegration rate with other studied nitro esters, whose melting point is much lower, it was expedient to conduct experiments at temperatures above the melting point of PETN, i. e. with its melt. By the usual unautomatized method this is possible to realize in a temperature range from 141° to approximately 170°. At higher temperatures decomposition on the one hand goes too fast, and on the other hand half-life becomes commensurable with the heating time of the vessel.

Experiments were conducted with moderate filling of reaction vessel δ, in order to make it possible to observe the course of disintegration not only at its beginning stages. Curves of gas formation - time and rate of gas formation - time in range of temperatures 145 - 171° (fig. 5) show that the general progress of disintegration is similar to that, which is observed for other nitro esters (nitroglycerine, nitroglycol, nitrocellulose). Gas formation starts immediately after location of reaction vessel in thermostat and continues with increasing speed, and after passing through a maximum it decreases. The gas phase acquires a yellow color, intensity of which passes through maximum and disappears toward the end of disintegration.

As was observed for nitroglycerine and nitroglycol with an increase of δ the initial rate of gas formation somewhat decreases. In a region of small δ this phenomenon develops more strongly. Thus at 145° initial gas formation rate with $\delta = 3 \cdot 10^{-4}$ constituted 0.62 n $cm^3/g \cdot min$, and with $\delta = 45 \cdot 10^{-4}$ it equaled 0.45 n $cm^3/g \cdot min$(see table 3 and fig. 6). Curves of gas formation, rate time with various δ, shown in fig. 6, indicate that maximum of rate also decreases with increase of δ. It is necessary to mention however, that this is correct only for small δ, when the pressure of disintegration products is not great and their accelerating action is not developed, and when deceleration begins rapidly because of decrease of substance.

Similarity of melted PETN with nitroglycerine and nitroglycol is observed also with respect to the effect of δ on the stage of acceleration of disintegration. The greater the δ, the more sharply expressed this acceleration. For this reason during large δ acceleration manages to quickly compensate lag of speed in initial stages until disintegration begins to be delayed due to decrease of substance and the rate gradually becomes greater than during small δ. This shows that acceleration in decomposition of nitro ester depends on pressure of gasiform disintegration products or, more accurately, on their concentration in condensed phase, since according to Henry's law this concentration is proportional to pressure.

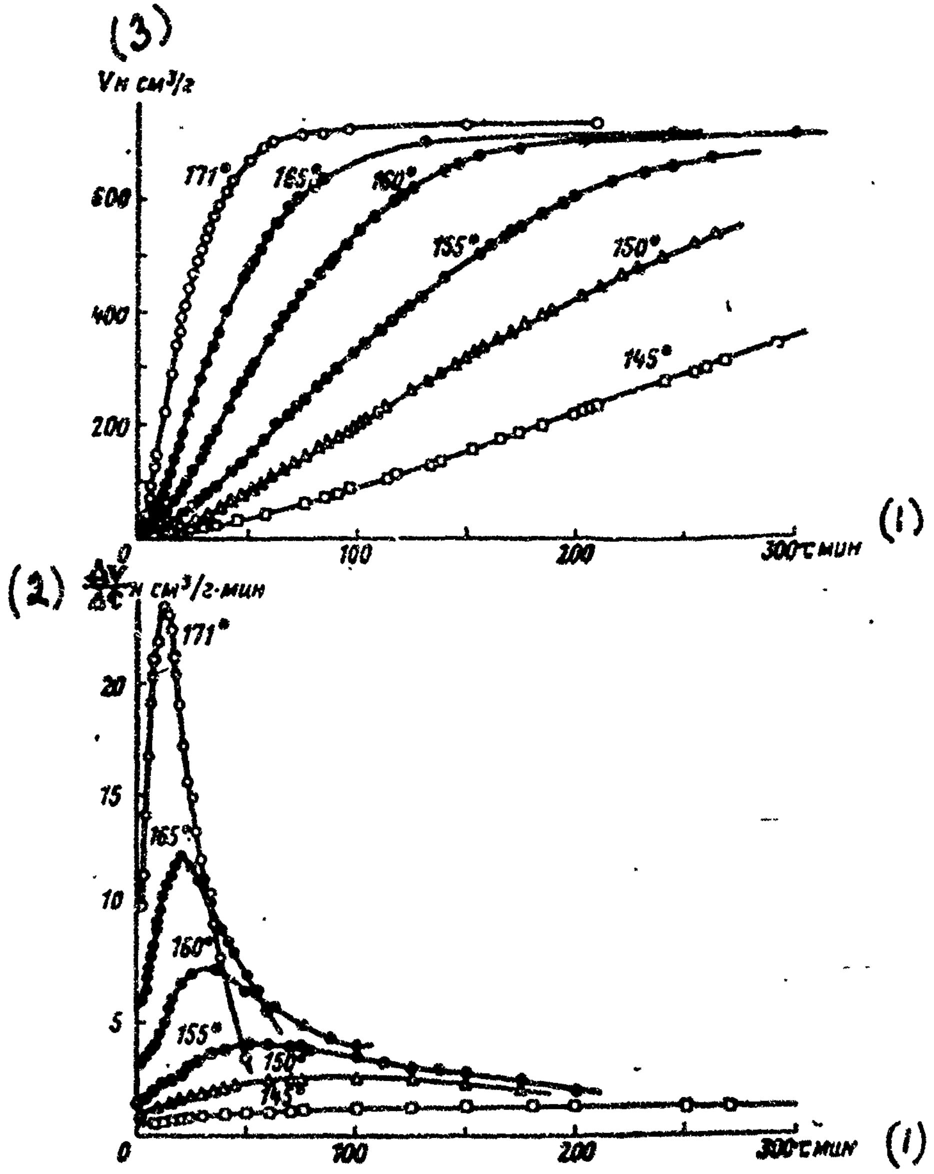

Fig. 5. Change of gas formation and its rate in time during disintegration of PETN in melt in a temperature range of 145 - 171° and $\delta = 11 \cdot 10^{-4}$.
1)τminutes; 2)$\frac{\Delta V}{\Delta \tau}$ n cm^3/g · min; 3) V n cm^3/g

The reason for the effect of δ on initial disintegration rate is less clear.

Fig. 6 for comparison presents the decomposition curve of nitroglycerine. As can be seen from graphs and table 3, PETN in liquid phase is decomposed at a temperature of 145° approximately 2 times slower than nitroglycerine.

Table 3

Initial disintegration rate of PETN and certain other nitro esters at 145° and 140° and different degrees of filling of vessel (δ)

(1) ВВ	t °C	m г (7)	$V_{p.c}$ см³ (8)	δ·10⁴	(9) $w_{нач}$ нсм³/г·мин	(10) $w_{тэн\ нач}/w_{ВВ\ нач}$
(2) Тэн	145	0,0112	22,12	2,9	0,62	—
(2) Тэн	.	0,0442	22,13	11,8	0,53	—
(2) Тэн	.	0,1419	22,65	36,4	0,49	0,49
(2) Тэн	.	0,1798	22,06	46,4	0,45	0,45
(3) НГЦ	.	0,1414	20,12	43,6	1,00	—
(2) Тэн	.	0,7173	151,30	27,1	0,45	—
(2) Тэн	.	0,0269	5,74	26,7	0,55	0,48
(3) НГЦ	.	0,0229	4,78	29,8	1,15	—
(2) Тэн (4) (60%-ный раствор в ТНТ)	140	0,0487	9,21	30,2	0,28	0,48
(3) НГЦ	.	0,0372	5,99	38,7	0,58	—
(5) НГЛ	.	0,0844	18,38	30,5	0,19	1,48
(6) ДГДН	.	0,0230	6,04	27,3	0,098	2,92

m - weighed amount of explosive substance; $V_{p.c}$ - volume of reaction vessel; w - rate of gas formation.

1) explosives substance; 2) PETN; 3) nitroglycerine (NG); 4) (60% solution in TNT; 5) NGL; 6) DGDN; 7) g; 8) $V_{p.c}$ cm³; 9) $w_{initial}$, n cm³/g·min; 10) ($w_{PETN\ initial}$)/(w explosive initial); 11) Explosive substance initial.

In order to compare the decomposition of PETN with other nitro esters (ethyleneglycoldinitrate - NGL and diethyleneglycoldinitrate - DGDN) we selected as the temperature 140° (fig. 7). It is true, at a temperature of 140°, PETN in the beginning of the experiment has to be in solid state, but, as the experiments conducted, showed, PETN undergoes fast progressive melting. Thus, in the experiment with $\delta = 55 \cdot 10^{-4}$ 12 minutes after submersion in thermostat, it was observed that condensed phase was partially melted, and after 28 minutes it was already completely liquid. The progressive melting of PETN can be seen also on graphs, where the noticeable acceleration in initial sections of disintegration can be easily seen.

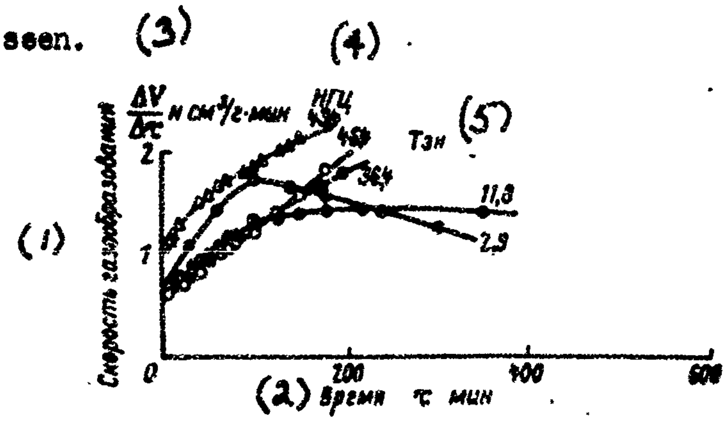

Fig. 6. Effect of δ on gas formation rate during disintegration of melted PETN at 145°. Numbers by curves are values of $\delta \cdot 10^4$.

1) Gas formation rate; 2) time τ minutes; 3) $\frac{\Delta V}{\Delta \tau}$ n cm^3/g·min; 4) NG; 5) PETN.

From fig. 7 and table 3 it is clear that the disintegration rate of PETN at 140° occupies an intermediate position between decomposition rates of nitroglycerine and nitroglycol. In the beginning of decomposition it is less by a factor of 2 than for nitroglycerine, one and a half times more than for nitroglycol, and approximately three times more than for disthyleneglycoldinitrate.

For a reliable comparison of disintegration of PETN at 140° with the above mentioned nitro ester, it is necessary that from the very beginning of the experiment PETN be in liquid state. This condition we ensure by dissolving PETN in a solvent inert at this temperature - trotyl.

In the initial stages of disintegration in the case of pure PETN the rate is approximately 0.10 n cm^3/g, while in the case of solution it is noticeably higher - 0.28 n cm^3/g · min. Later with progressive melting the rate in the first case increases, attaining the value of the decomposition rate of solution, which at large values of δ becomes higher, thus it also must be due to the effect of the degree of filling on the stage of disintegration acceleration.

The course of disintegration of PETN during various temperatures, as graphs in Fig. 5 show, has in general a similar character. One may see this more graphically from fig. 8, where curves $V = 4f(\tau)$ are represented in combined view.

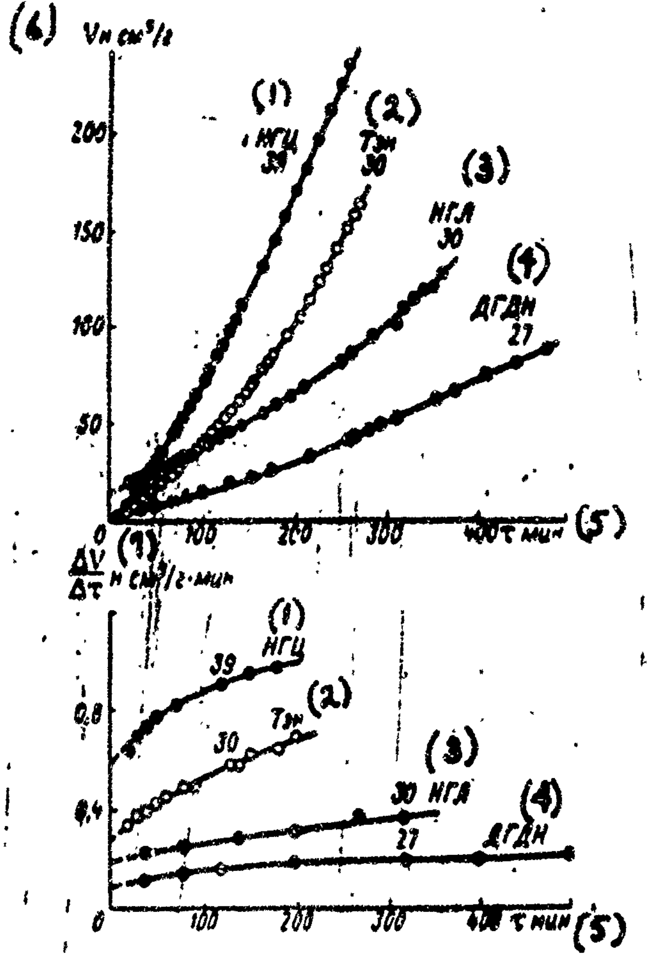

Fig. 7. Comparison of thermal disintegration of PETN, nitroglycerine, ethyleneglycoldinitrate and diethyleneglycoldinitrate at 140°. (Numbers by curves $-\delta \cdot 10^4$).

1) NC; 2) PETN; 3) NGL; 4) DGDN; 5) τ Minute; 6) V n cm^3/g; 7) $\Delta V/\Delta \tau$ n $cm^3/g \cdot min$.

In a considerable part of the disintegration a change of time scale leads to a good combination of curves in all the temperature range from 145 to 171°. Absolute rate gas formation grows until it attains approximately 30% V_{end}; its magnitude at maximum 2.5 times exceeds initial value, after which deceleration starts.

By the dependence of the transformation coefficient on temperature it is possible to calculate magnitude of activation energy. Corresponding data, drawn in fig. 9 and presented in table 4, fall well on straight line and give E = 39,000 cal/mole. If in the intial stage we consider disintegration monomolecular, then the constant of disintegration rate, calculated from initial rate of gas formation at 160° constitutes $6.86\cdot10^{-5}$ $\sec^{-1}$. Pre-exponential multiplier in Arrhenius equation is equal to $10^{15.6}$ $\sec^{-1}$.

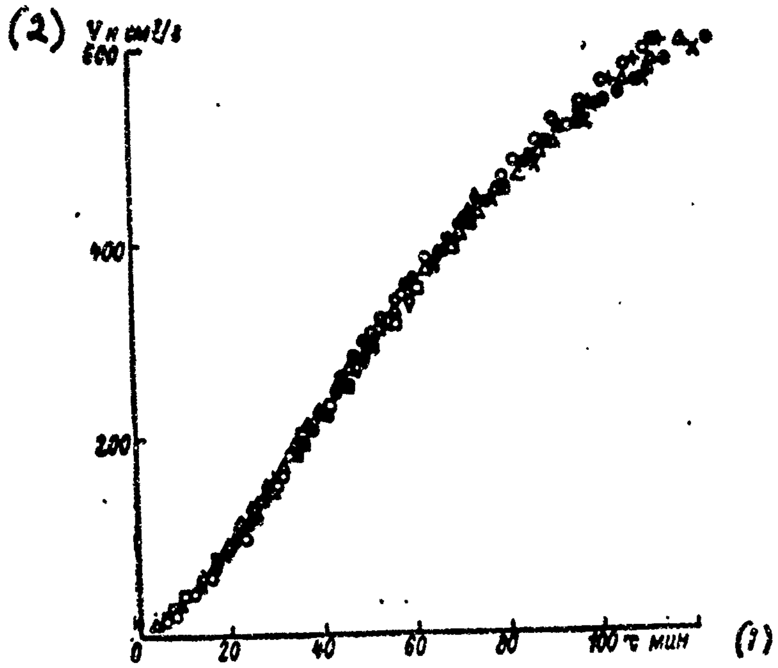

Fig. 8. Combination of curves of thermal decomposition of PETN in a temperature range of 145 - 171° and $\delta \approx 11\cdot10^{-4}$.

1) τ Minute; 2) V n cm^3/g.

Fig. 9. Dependence of logarithm of coefficient of combination K curves $V = f(\tau)$ on reverse temperature.

1) lg K combined.

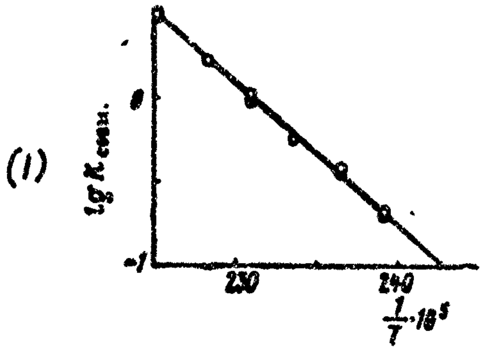

Table 4

Dependence of disintegration rate of PETN on temperature.

$\delta \cdot 10^4$	t °C	$\frac{1}{T} \cdot 10^5$	$K_{\text{совм}}$*	lg $K_{\text{совм}}$
10,8	171	225,2	3,14	0,497
11,4	171	225,2	3,32	0,521
11,3	171	225,2	3,19	0,504
11,1	165	228,3	1,69	0,228
10,8	160	230,9	1,05	0,021
10,5	160	230,9	1,00	0,000
11,6	155	233,6	0,572	—0,243
10,8	150	236,5	0,373	—0,427
10,8	150	236,5	0,368	—0,434
11,8	145	239,2	0,203	—0,693
11,8	145	239,2	0,200	—0,699

---

* K combined = τ 160°/τt°.

Disintegration of PETN in Trotyl Solutions

The investigation of the disintegration of PETN in solutions pursued three main goals. By comparing the disintegration rate of melt of PETN and its solution in trotyl, it would have been possible to establish, whether trotyl affects the disintegration of PETN and what is the character of this effect. Changing the concentration of PETN in solution, could explain, how it affects the disintegration rate and, thus, establish sequence of leading reactions during the disintegration of PETN. At last, study of decomposition of solutions would allow us to significantly expand the temperature range in the investigation of thermal disintegration of PETN in liquid state in region of temperatures lower than the melting point of PETN.

Comparative data on disintegration of melt of PETN and its solutions in trotyl at 145° are presented in table 5 and represented in fig. 10[1]. It is clear

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[1] For experiments on disintegration of PETN in trotyl solutions δ was calculated as ratio of volume of weighed amount of PETN to sum of volumes of free space and weighed amount.

that trotyl not only does not increase the disintegration rate of PETN, but on the contrary somewhat lowers it. Thus, during transition from melt to 40% solution the rate decreases by 10-15%; for 5% solution it constitutes nearly 2/3 decomposition rate of melt. However this decrease in rate with concentration is too small to make it possible to draw conclusions concerning the bimolecularity of the leading reaction, and is connected, apparently, with delay of subsequent reactions or with interaction of gasiform products of disintegration of PETN with trotyl, proceeding with decrease of volume. It is very possible also that gasiform products of disintegration are soluble in trotyl, which causes the apparent decrease in their quantity.

Table 5

Dependence of disintegration rate of solutions of PETN in trotyl at 145° on concentration

$\delta \cdot 10^4$	(1) Концентрация тэна в растворе % вес.	(2) $w_{нач}$ н $см^3/г \cdot мин$	(3) $\frac{w_{тэн+ТНТ\ нач}}{w_{тэн.нач}}$	(4) $w_{\tau=100\ мин.}$	(5) $\frac{w_{тэн+ТНТ}}{w_{тэн}}$
36,4	100	0,49	—	1,20	—
31,8	39	0,42	0,86	1,11	0,92
30,7	5	0,30	0,61	0,82	0,68
11,9	100	—	—	1,26	—
16,4	13	—	—	0,89	0,71

1) Concentrations of PETN in solution % weight;
2) $w_{initial}$, n $cm^3/g.$ min; 3) $(W_{PETN+TNT\ initial})/(w_{PETN\ initial})$; 4) $w_{\tau = 100\ min.}$; 5) $(w_{PETN+TNT})/w_{PETN}$;

Fig. 11 presents results of experiments on disintegration of 50% solutions of PETN in trotyl at 120° and various δ.

As at 145° an increase in the degree of filling of vessel δ leads to some decrease in the gas formation rate in the initial stage of disintegration. Thus, for instance, the initial gas formation rate at $\delta = 70 \cdot 10^{-4}$ is 0.0218 n $cm^3/g \cdot min$, while at $\delta = 273 \cdot 10^{-4}$ it is 0.015 n $cm^3/g \cdot min$.

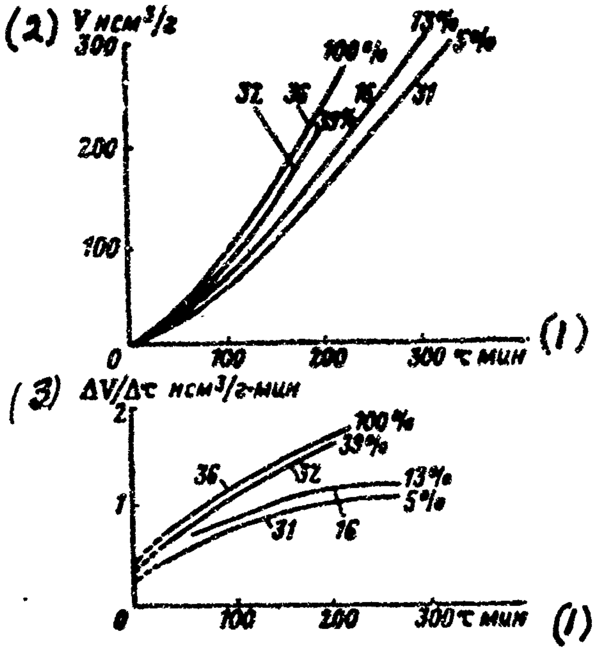

Fig. 10. Effect of concentration on gas formation and its rate during disintegration of PETN in trotyl solutions at 145°. Numbers by curves - % of PETN in trotyl and $\delta \cdot 10^4$.

1)τ minute; 2) V n cm^3/g. 3)$\Delta V/\Delta \tau$,n cm^3/g. min:

The general picture of the development of gas liberation is similar to that, which was observed during disintegration of nitroglycerine. On the graph two stages of decomposition are clearly noticeable: the initial stage with slowly growing gas formation rate and the stage of its rapid growth, the earlier the onset, the bigger the δ , i. e. pressure of gasiform disintegration products.

The course of the disintegration of 5% solutions of PETN in trotyl at 100° has a similar character, as may be seen from graphs in fig. 12 and 13.

Transition from first stage to second is even more graphically seen in fig. 14 and 15, depicting in logarithmic coordinates the dependence of gas formation rate on pressure at 100 and 120°. The curve of each experiment can be represented, as consisting two straight lines, proceeding under various angles of inclination and correspondingly reflecting two stages of the decomposition process; initial, when disintegration rate slightly depends on pressure, and second stage, when rate depends on it considerably more sharply.

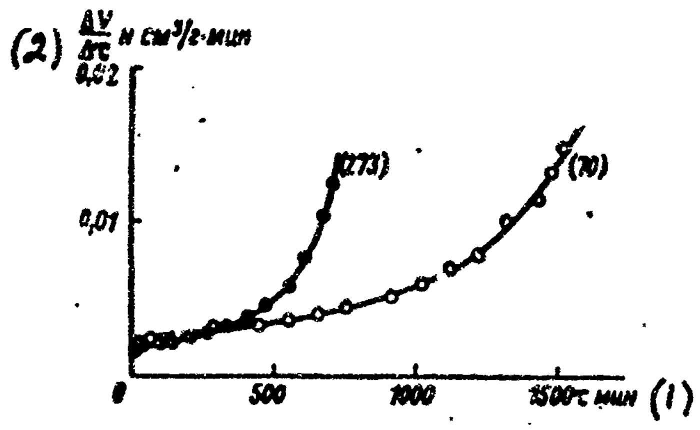

Fig. 11. Change of gas formation rate in time during disintegration of PETN in 50% trotyl solutions at 120° and different δ. Numbers by curves - $\delta \cdot 10^4$.

1) τ minute; 2) $\Delta V/\Delta\tau$ n cm^3/g·min.

Table 6 presents coefficients of the equation, expressing linear relationship between logarithms of rate and pressure: $\lg w = \lg A + B \lg p$ in the second stage of disintegration. At 100° just as in the case of nitroglycerine, the gas formation rate in the second stage grows proportionally to the pressure, approximately in the second degree.

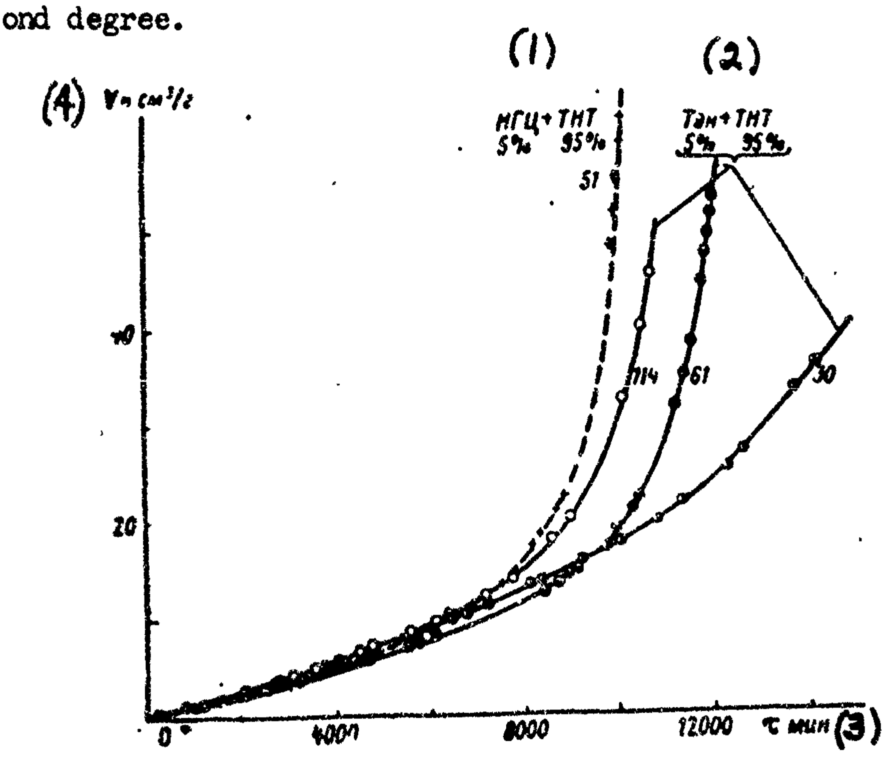

Fig. 12. Decomposition of PETN and nitroglycerine in 5% trotyl solutions at 100°. Numbers by curves $-\delta \cdot 10^4$.

1) NG+TNT; 2) PETN+TNT; 3) τ minute; 4) V n cm^3/g.

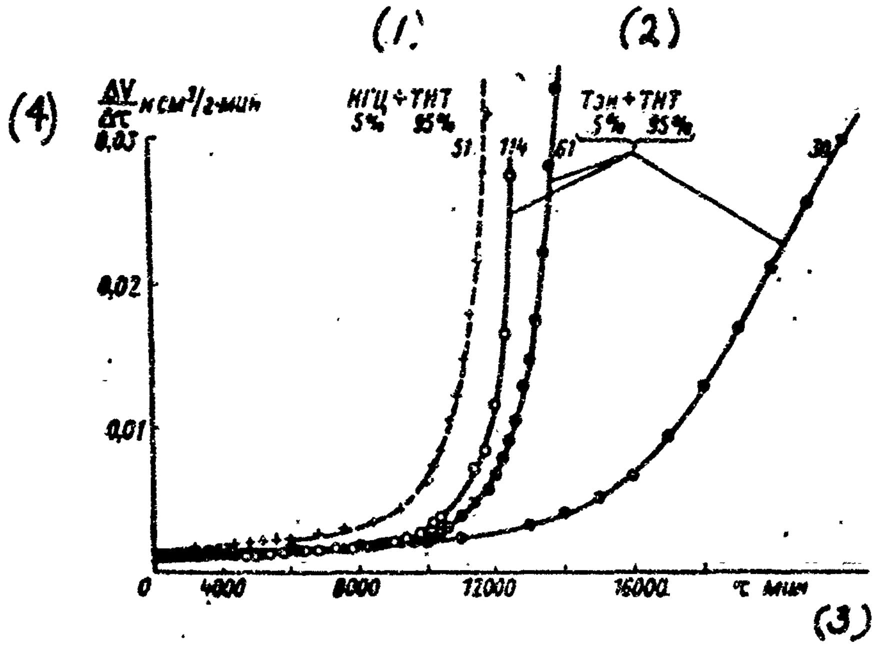

Fig. 13. Change of gas formation rate in 5% solutions of PETN and nitroglycerine in trotyl with time at 100° and different δ. Numbers by curves - $\delta \cdot 10^4$.

1) NG+TNT; 2) PETN+TNT; 3) τ minute; 4) $\Delta V/\Delta \tau$ n cm^3/g min.

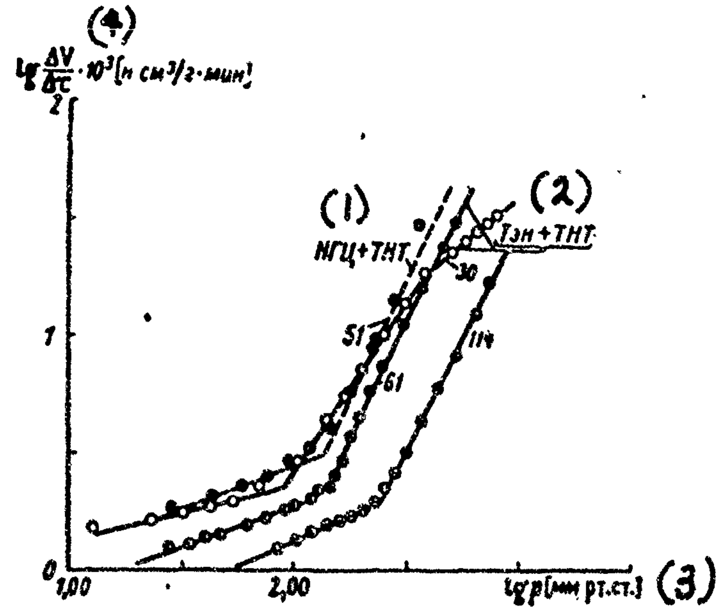

Fig. 14. Dependence of lg w on lg p during disintegration of 5% solutions of PETN and nitroglycerine in trotyl at 100° and different δ. Numbers by curves - $\delta \cdot 10^4$.

1) NG+TNT; 2) PETN+TNT; 3) lg p [mm of mercury]; 4) $\Delta V/\Delta \tau \cdot 10^3$ n cm^3/g · min.

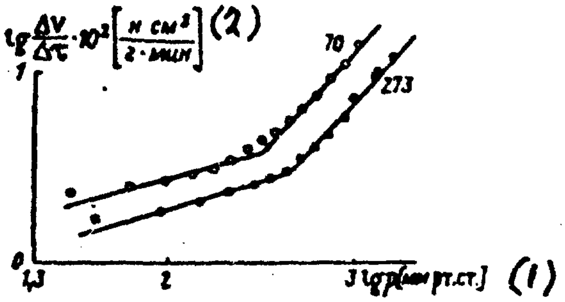

Fig. 15. Dependence of lg w on lg p during disintegration of 50% solutions of PETN in trotyl at 120° and different δ. Numbers by curves – $\delta \cdot 10^4$.

1) lg p [mm of mercury]; 2) $\left[\frac{\text{n cm}^3}{\text{g} \cdot \text{min.}}\right]$

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Table 6

Dependence of disintegration rate of PETN, nitroglycerine and their solutions in trotyl on pressure at 100 and 120°

t°C (1)	(2) ВВ	Содержание нитроэфира в растворе % вес. (3)	$\delta \cdot 10^4$	lg A	B
100	(4) Тэн	5	30,0	—5,39	1,40
	Тэн	5	60,7	—6,84	1,94
	Тэн	5	114,0	—7,27	1,90
	(5) НГЦ	5	51,0	—6,78	1,99
	НГЦ	(6) чистый	29,0	—	2,4
	НГЦ	»	655,0	—	2,2
120	(4) Тэн	50	70,0	—5,10	1,06
	Тэн]	50	273,0	—5,30	1,04
	(5) НГЦ	(6) чистый	75,5	—	2,0
	НГЦ	»	216,0	—	2,1

1) t °C; 2) Explosive substances; 3) Contents of nitro ester in solution % weight; 4) PETN; 5) NG; 6) Pure

At 120°, however, the disintegration rate of PETN in trotyl solution in the second stage grows proportionally to the first degree of pressure, while in the case of pure nitroglycerine with the same temperature it grows proportionally to the square of pressure.

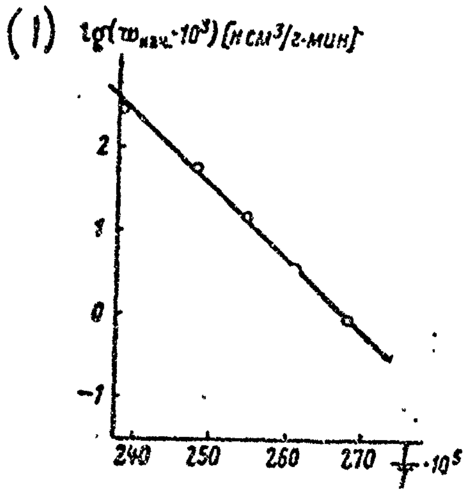

Fig. 16. Dependence of lg w_{initial} on 1/T during decomposition of PETN in trotyl solutions in a temperature range of 100 - 145°.

1) $\lg(w_{\text{initial}} \cdot 10^3)$ [n cm³/g min]

By the extrapolation of curves $w-\tau$ for time, equal to zero, initial gas formation rates were determined in a range of 100 - 145° for disintegration of 5% solutions of PETN in trotyl (see table 7). Magnitude of activation energy, determined by angle of inclination of straight line $\lg w_{\text{initial}} - \frac{1}{T}$ (fig. 16), equals 40,100 cal/mole, i. e. practically the same as for melt at 145 - 171°. If one were to consider disintegration monomolecular in the initial stage, then the constant of rate at 110° constitutes $8.57 \cdot 10^{-8}$ $\sec^{-1}$, and the pre-exponential multiplier in Arrhenius equation is equal to $10^{15.8}$ $\sec^{-1}$.

Table 7

Dependence of disintegration rate of solutions of PETN in trotyl on Temperature

t° C (1)	$\frac{1}{T} \cdot 10^5$	$\tau \cdot 10^4$	Содержание тэна в растворе (2) % вес.	(3) $w_{нач} \cdot 10^3$ в $см^3/г \cdot мин$	(4) lg ($w_{нач} \cdot 10^3$)
100	268,1	60,7	5,5	0,93	−0,032
110	261,1	303,0	20,0	3,75	0,574
120	254,4	46,7	4,5	15,50	1,193
130	248,1	59,0	5,8	58,00	1,764
145	239,2	30,7	5,0	300,00	2,477

1) t °C; 2) Contents of PETN in solution % weight; 3) w initial $\cdot 10^3$, n cm^3/g. min; 4) log (w initial $\cdot 10^3$)

Disintegration of PETN in Solid State

If PETN in melt or in trotyl solution is decomposed with a rate of the same order as nitroglycerine, then the disintegration of solid PETN proceeds both in the beginning, and after onset of acceleration much more slowly. A presentation of the difference in the rates of solid and liquid PETN at 120° is given by the graphs in Fig. 17 and Table 8.

Table 8

Characteristics of the course of disintegration in solid PETN and its trotyl solutions at differ-

(1) t °C	з $\cdot 10^4$	Агрегатное состояние ВВ (2)	$w_{нач} \cdot 10^3$ н см³/г·мин (8)	$\frac{w_{ж.нач}}{w_{тв.нач}}$ (9)	$w_5 \cdot 10^3$ н см³*/г·мин (10)	$\frac{w_5}{w_{нач}}$ (11)	$\frac{1}{T} \cdot 10^5$	$\lg(w_{нач} \cdot 10^3)$ (12)
110	875	(3) твердый	0,038	99	0,99	26	261,1	—1,420
120	875	»	0,230	65	17,60	76	254,4	—0,638
130	279	»	1,45	40	34,50	24	248,1	0,161
135	52	»	4,50	—	90,00	20	245,1	0,653
140	55	»	100,00	2,8	318,00	3,2	242,2	2,000
110	303	(4) 20%-ный раствор	3,75	—	7,90	2,1	—	
120	272	(5) 50%-ный раствор	15,00	—	24,50	1,6	—	
130	59	(6) 6%-ный раствор	58,00	—	73,00	1,3	—	
140	25	(7) 60%-ный раствор	280,00	—	342,00	1,2	—	

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* w_5 — скорость в момент выделения 5 н см³/г газа.

* w 5 - rate at monent of liberation 5 n cm^3 /g of gas.

1) t °C; 2) Aggregation state of explosive substances; 3) Solid; 4) 20% solution; 5) 50% solution; 6) 6% solution; 7) 60% solution; 8) $w_{initial} \cdot 10^3$, n cm^3/ g. min; 9) $(w_{liq\ initial})/(w_{solid\ initial})$; 10) $w_5 \cdot 10^3$, n cm^{3*}/g. min; 11) $w_5/w_{initial}$; 12) log $(w_{initial} \cdot 10^3)$

Initial disintegration rate of solid PETN at 120° is 65 times less for PETN in solution and approximately 130 times less than for pure nitroglycerine. As in the case of liquid PETN on the curves of gas formation for solid matter it is possible to distinguish 2 stages: initial, with comparatively slow growth of gas formation rate and the stage of its fast growth in time.

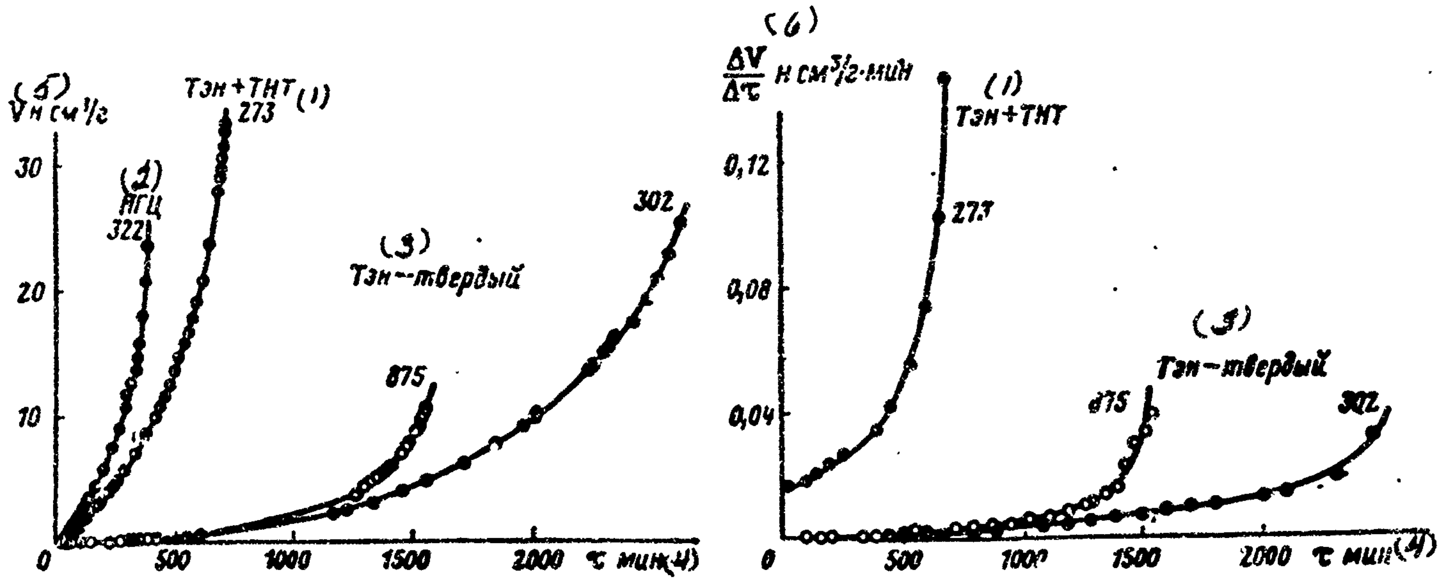

Fig. 17. Change of gas formation and its rate in time during disintegration of solid PETN and PETN in trotyl solution at 120°. Number by curves - $\delta \cdot 10^4$.

1) PETN+TNT; 2) NG; 3) PETN-solid; 4) minutes; 5) V cm³/g.

Characteristic for decomposition of solid PETN is the strong acceleration of gas formation depending upon the degree of disintegration. Thus, for example, before liberation of 5 cm³/g of gas the gas formation rate in the case of disintegration of solid PETN increases approximately 40 times, while during decomposition of PETN in trotyl solution it increases only 1.6 times. A similar case was observed by Farmer [11] during the study of disintegration of tetryl. For explanation of this fact he assumed that there occurs progressive melting of solid substance in the course of its disintegration.

It must be noted that in all disintegration of solid PETN at 120°, and also in experiments at 110 and 130° the appearance of melt was not detected upon fast removal of the instrument from the thermostat and examining of crystals by the naked eye or magnifier, apparently because of its insignificant quantity, although decomposition was brought up to liberation of 25 and 55 n cm^3/g of gases. However at temperatures, near the melting point, for example, 135°, we must qualitatively observe progressive melting of PETN.

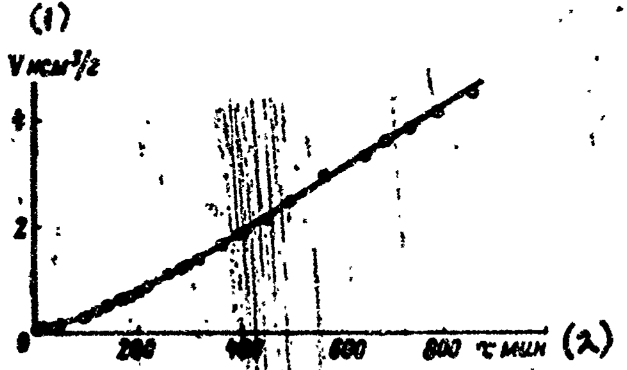

Fig. 18. Change of gas formation in time during disintegration of solid PETN at 110° and $\delta \cdot 10^4 = 875$.

1) V n cm^3/g; 2) minute

Thus, upon attaining 2.7% decomposition of parent substance (~ 20 n cm^3/g of gases) presence of a liquid phase was not noticed, but on the walls of the vessel during its cooling the formation of new, very fine needle small crystals, was observed and the old large crystals no longer had the initial sharp outlines. Later during 3.7% decomposition (~ 27 n cm^3/g gases) all these phenomena were observed even more sharply, the outlines of the old crystals were hardly noticeable and the substance formed a solid mass. Full melting set in approximately during 6% decomposition of substance liberation of (~ 45 n cm^3/g of gases). At 140° full melting was observed much earlier, namely, during decomposition of only 1% of substance liberation of (6 - 7 n cm^3/g of gases).

Results of the study of disintegration of solid PETN in a temperature range of 110 - 140° (see fig. 18, 19, 20 and table 8), point out the fact that in the growth of disintegration rate action appears to be not only a gradual transition of solid matter into liquid phase, but also a factor, determining the acceleration of the disintegration of liquid nitro ester, i. e. dissolving of gasiform products of disintegration in condensed phase.

If disintegration were accelerated only because of progressive melting, then at the moment of complete melting of substance the gas formation rate during disintegration of PETN lower than its melting point could not exceed initial disintegration rate of its solution.

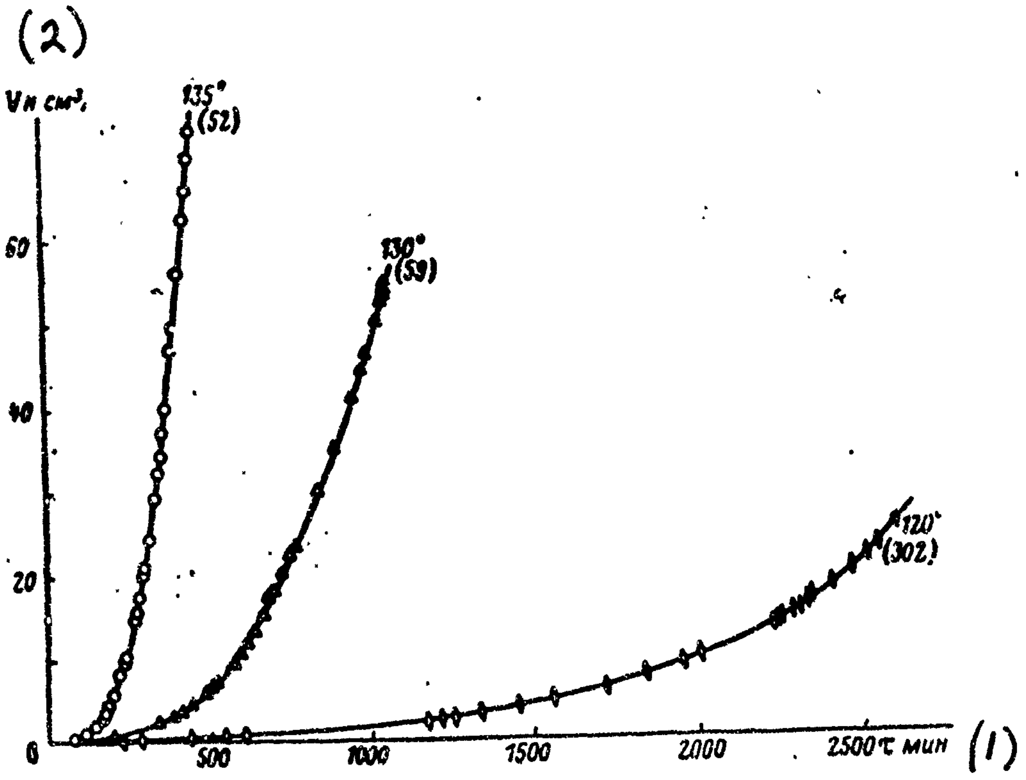

Fig. 19. Change of gas formation in time during disintegration of solid PETN at 120 - 135°. Numbers by curves - temperature of experiment in °C and $\delta \cdot 10^4$ (in parentheses).

1) minute; 2) V n cm^3/g.

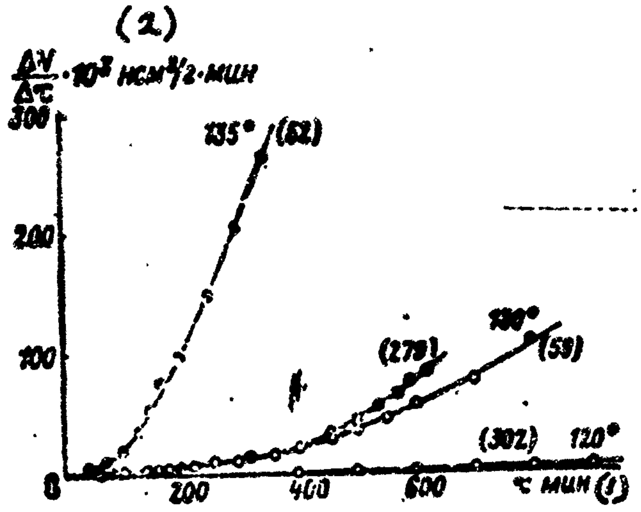

Fig. 20. Change of gas formation rate in time during disintegration of solid PETN in a temperature range of 120 - 135°. Numbers by curves - temperature of experiment in °C and $\delta \cdot 10^4$ (in parentheses).

1) minute; 2) $\Delta V/\Delta \tau \cdot 10^3$ n cm^3/g . min

But as fig. 17 shows, disintegration rate of solid PETN attains values at 120° two and more times exceeding initial disintegration rate of its solution with the same temperature, in spite of the fact that not only does full melting not occur, but also formation of melt is so insignificant that it was not noticed when examining the crystals with the help of a magnifier.

From graphs of Fig. 17 - 20 and table 8 it is clear that with an increase of temperature the difference in initial disintegration rates of solid PETN and its solution decreases and when approaching the melting point the ratio moves toward one.

The temperature coefficient of gas formation rate during disintegration of solid PETN is rapidly increased with increase of temperature and, therefore, if one were to construct graph $\lg w_{\text{initial}} - \frac{1}{T}$ (see fig. 21), then a lines with a clear curvature is obtained. All this points out the fact that using the usual method to calculate activation energy and B is in this case incorrect. If one were to calculate E by two points, corresponding to the lowest temperatures, then 51,500 cal/mole is obtained, but with two higher temperatures (130 - 135°) - 72,800 cal/mole.

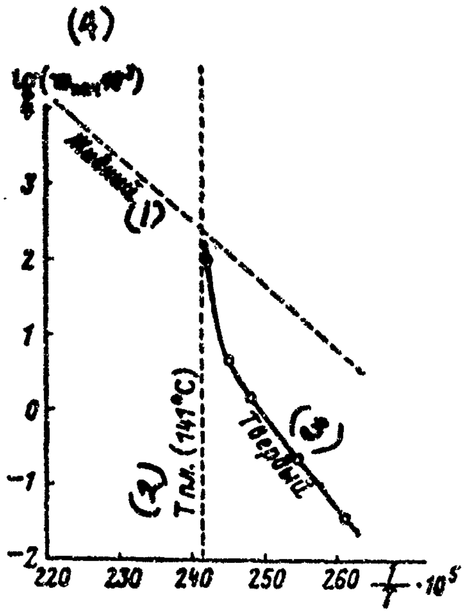

Fig. 21. Dependence of lg $w_{initial}$ on 1/T during disintegration of PETN in a temperature range of 110 - 171°.

1) Liquid; 2) Melting point 141°C; 3) Solid; 4) Log $w_{initial} \cdot 10^3$

These peculiarities of disintegration of solid PETN lead to the thought that there is, possibly a liquid phase, already in the very beginning of disintegration before the formation of noticeable quantities of the condensed product which transfers part of the substance into liquid state. It is possible to assume that in the appearance of liquid phase impurities contained by PETN in small quantities are at fault[1]. In such case the initial decomposition rate of PETN will grow with temperature faster, than according to Arrhenius law, because of an increase of solubility of substance with the rise of temperature the quantity of liquid phase will also be increased in impurities. If this is so, then the initial disintegration rates of PETN we obtained in solid state are total rates, composed of decomposition rate of solid substance (w_s) and decomposition rate of liquid PETN[2] (w_{liq}):

$$w_{otal} = \alpha w_{\ell} + (1-\alpha) w_s.$$

where α is the portion of liquid PETN.

This equation has two unknowns (α and w_s). For its solution it is necessary to determine one of these magnitudes.

However, disregarding in this equation term $(1 - \alpha) w_s$, i. e. taking conditionally that decomposition goes on only because of liquid phase, we can obtain the following limiting values of the quantity of the latter at various temperatures:

---

[1] Hinshelwood [13] during the investigation of the disintegration of solid tetryl also concludes that even after thorough purification tetryl, probably, still contains a small quantity of impurities, which, while causing the appearance of traces liquid phase, increase the initial rate of its decomposition.

[2] It is assumed that the decomposition rate of impurities equals zero.

$$(\alpha)_{110^\circ}=\frac{0,038}{3,75}=0,010 \quad \text{or} \quad 1,0\%;$$

$$(\alpha)_{120^\circ}=\frac{0,23}{15,0}=0,015 \quad \text{or} \quad 1,5\%;$$

$$(\alpha)_{130^\circ}=\frac{1,45}{58}=0,025 \quad \text{or} \quad 2,5\%;$$

$$(\alpha)_{140^\circ}=\frac{100}{280}=0,35 \quad \text{or} \quad 35\%.$$

It is clear without explanation that real values will be lower.

From table 8 it is also clear that the magnitude of acceleration of disintegration of solid PETN, i. e. the ratio of the rate at a definite degree of disintegration to its initial value with an increase of temperature passes through maximum. Here, apparently, is developed simultaneous action of two factors.

On the one hand, as we have seen above, with an increase of temperature the difference in initial disintegration rates of solid and liquid PETN decreases and the stronger the decrease, the nearer the melting point. Therefore, when approaching the latter, acceleration of the process of gas formation $(w_r/w_{\text{init.}})$ decreases and becomes near to acceleration during disintegration of liquid PETN.

On the other hand at low temperatures progressive melting of PETN, because of a significant decrease of its solubility in the condensed intermediate product of decomposition is expressed weakly. Therefore, in spite of the fact that the difference in disintegration rates of solid and liquid PETN at low temperatures is larger, the acceleration of gas formation still turns out to be insignificant. At a certain optimum temperature (between 110 - 130°) the effect of these two factors is the most favorable for maximum increase of acceleration of disintegration.

Disintegration of PETN in Vapor

The decomposition rate of nitroglycerine and nitroglycol in vapor is significantly more, than for liquid, and for nitroglycerine in this case there is not observed that acceleration of gas formation, which is characteristic for disintegration of liquid. It was of interest to study PETN in this respect. When calculating maximum degree of filling, with which the liquid phase is still absent, we used the data of A. F. Belyaev [2] concerning vapor tension of PETN. For 171° vapor tension of PETN obtained was 6.75 mm of mercury and limit value.

$$\delta = \frac{273\cdot 316\cdot 6,75}{760\cdot 444\cdot 22\,400\cdot 1,75} = 0,45\cdot 10^{-4}.$$

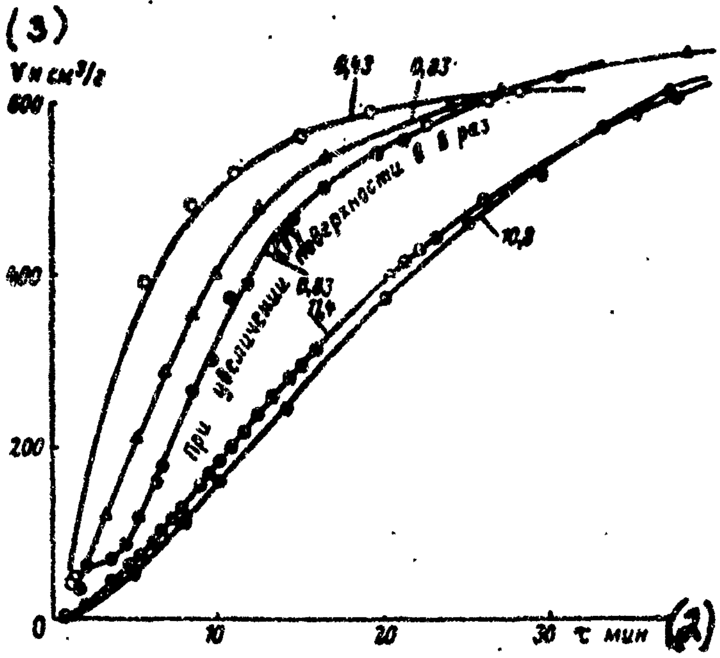

Fig. 22. Disintegration of PETN at 171° and different δ. Numbers by curves – $\delta \cdot 10^4$.

1) With an increase of surface 8 times; 2) minute; 3) V n cm³/g

On graphs of Fig. 22 and 23 are given curves of gas formation at 171° and various δ. Initial rates for three different δ are, respectively:

for $\delta = 11.4\cdot10^{-4}$ 17.9 n $cm^3/g\cdot min$;

for $\delta = 0.83\cdot10^{-4}$ 48.6 n $cm^3/g\cdot min$;

for $\delta = 0.43\cdot10^{-4}$ 88.4 n $cm^3/g\cdot min$;

Our attention is drawn to the fact that the gas formation rate considerably depends on δ , increasing with its decrease. This, apparently, basically is caused by the fact that the reaction rate in gas phase, a portion of which is increased with decrease of δ , is significantly more, than in liuqid. A second peculiarity of transformation during small δ is the fact that part of the acceleration is reduced, and with $\delta = 0.43\cdot10^{-4}$ is practically absent, similar to that which is observed for nitroglycerine.

If one were to accept, in accordance with the above, that at $\delta = 0.43\cdot10^{-4}$ all PETN is in vapor, and to compare the initial disintegration rate during different δ , then calculation leads to the conclusion that PETN in vapor is decomposed 6 - 8 times faster, than in liquid state.

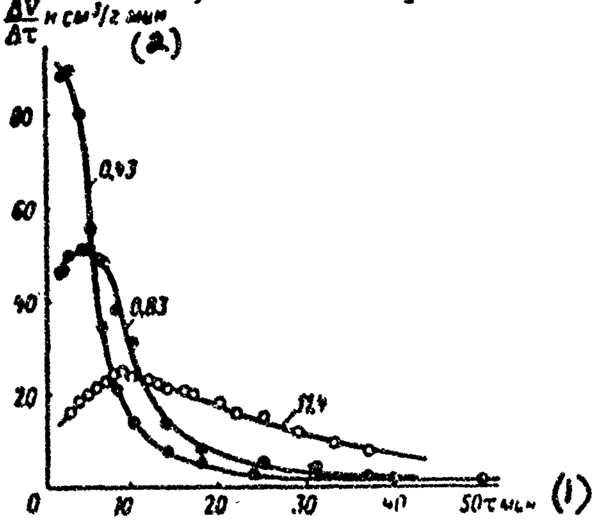

Fig. 23. Change of gas formation rate in time during disintegration of PETN at 171° and different δ . Numbers by curves $\delta\cdot10^4$.

1) minute; 2) $\Delta V/\Delta\tau$ n cm^3/g min

Experiments were also conducted with filling of the ampule by glass capillaries; this was not reflected on the magnitude of the rate which indicates (differing from nitroglycerine) an absence of noticeable heterogeneous reaction on walls of vessel.

Influence of Water and Oxygen on Disintegration of PETN

The strong and unique effect of water on disintegration of nitroglycerine [3], nitroglycol and other nitro esters is known.

Corresponding experiments were set up at 110 - 120° also for PETN in the form of its solution in trotyl (fig. 24 and 25). As in the case of nitroglycerine, in the beginning of the experiment a lowering of pressure is observed, but the character of this decrease in both cases is somewhat different. While in experiments with nitroglycerine on a section of the pressure - time curve there is an area of practically constant pressure, after which its fast drop begins, in the case of PETN the area is inconspicuous, and pressure decreases more smoothly. Increase of initial vapor pressure of water increases depth of drop on graph and more strongly accelerates process of gas formation, reducing the time to the beginning of sharp acceleration of disintegration. To explain the nature of this drop experiments were conducted on the dissolution of vaporous water in melted trotyl at 110 - 120°. As can be seen from fig. 24 and 25, the curve of pressure decrease almost exactly follows the path of the curve for disintegration of a solution of PETN in trotyl in the presence of water. This indicates that, the main cause of the appearance of the drop is dissolution of water vapor in liquid phase.

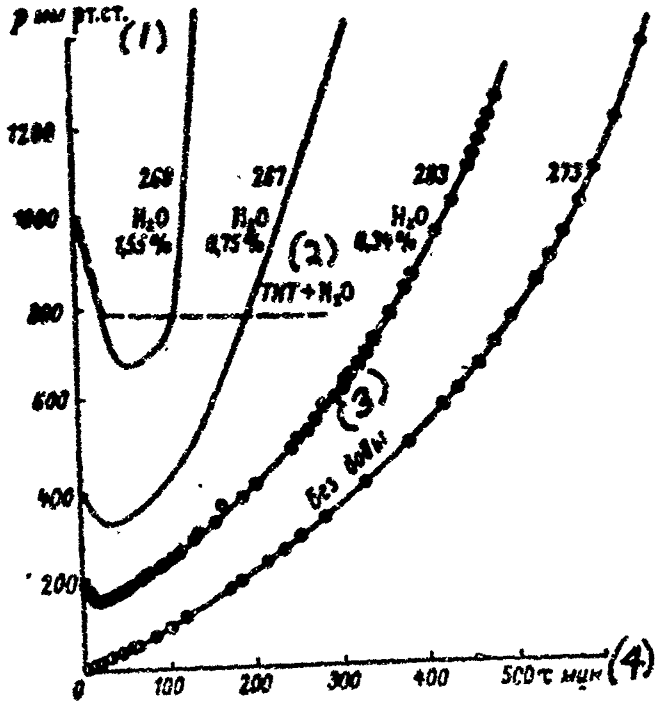

Fig. 24. Decomposition of PETN in trotyl solution in presence of water at 120°. Numbers by curves – $\delta \cdot 10^4$.

1) p mm of mercury; 2) TNT+H_2O; 3) Without water; 4) τ minute

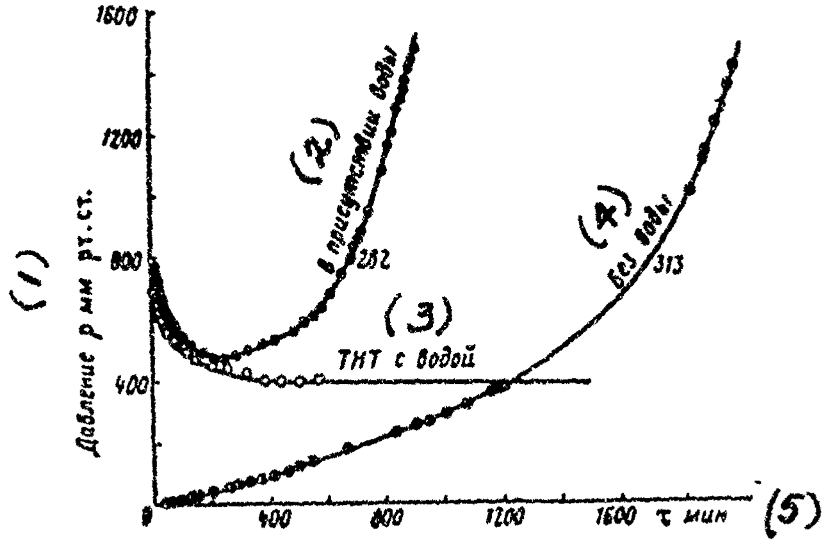

Fig. 25. Decomposition of PETN in trotyl solution in presence of water at 110°. Numbers by curves – $\delta \cdot 10^4$.

1) Pressure p mm of mercury; 2) In the presence of water; 3) TNT with water; 4) Without water; 5) τ minute.

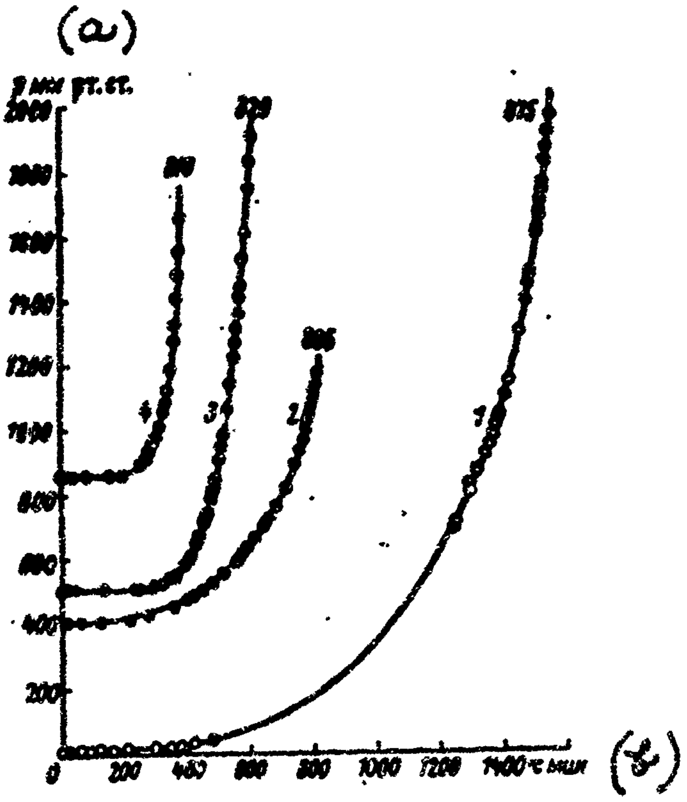

Fig. 26. Decomposition of solid PETN in the presence of water and oxygen at 120°.

1 - pure PETN; 2 - in presence of oxygen (PO_2 = 402 mm of mercury) 3 - in presence of water (p_{H_2O} = 504 mm of mercury); 4 - in presence of water and oxygen (p_{O_2} = 402 mm of mercury; P_{H_2O} = 454 mm of mercury. Numbers by curves - $\delta \cdot 10^4$.

a) p mm of mercury; b) τ minute

Results of the investigation on the effect of water on disintegration of solid PETN at 120° are shown in fig. 26. For nearly four hours pressure remains constant, while during disintegration of the substance without water during that time the pressure grew to 15 mm of mercury. From the graph it is clear that water two and more times reduces the induction period before onset of sharp acceleration of disintegration and leads to a more vigorous increase of the rate in this stage.

Experiments on disintegration of liquid PETN in the presence of oxygen (fig. 27) showed that oxygen does not affect rate of gas formation in initial stage of disintegration, but reduces time to onset of sharp acceleration. Oxygen exerts a similar influence also during disintegration of solid PETN (fig. 26).

The time to onset of sharp acceleration is especially strongly reduced during the joint presence of water and oxygen (curve 4).

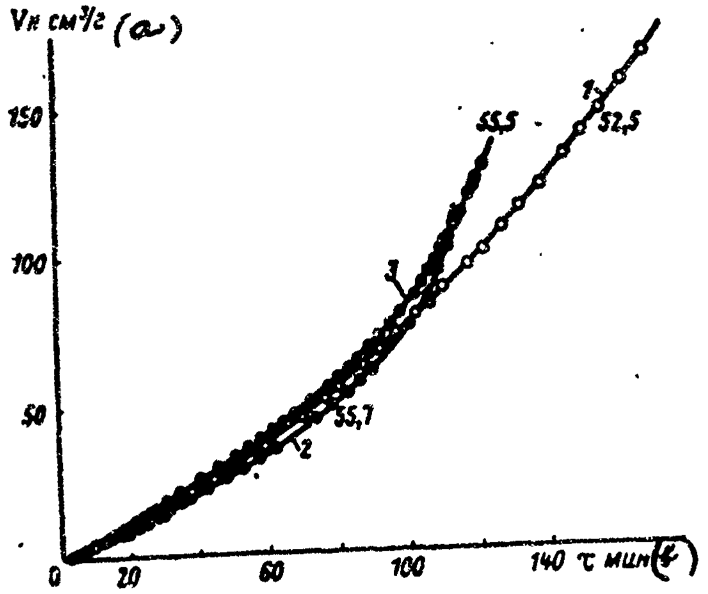

Fig. 27. Decomposition of melt of PETN in the presence of oxygen at 145°.

1 - pure PETN; 2 - in the presence of oxygen at p_{O_2} = 1930 mm of mercury; 3 - the same at p_{O_2} = 324 mm of mercury. Numbers by curves - $\delta \cdot 10^4$.

a) V n cm^3/g; b) τ minute

Discussion of Results

The data obtained on the disintegration rate of PETN at different temperatures, both above and below melting point, show the groundlessness of ideas that the increased stability of PETN is determined by peculiarities of its chemical structure. If one were to exclude the effect of the state of aggregation, i. e. to compare liquid PETN with other liquid nitro esters, then their disintegration rates turn out to be very close just as the main kinetic characteristics. This circumstance is not surprising, since the primary stage during disintegration of nitro ester is considered a breakaway of the NO_2 - group, but to expect essential distinctions in activation energy of this process for such substances, as for example, methylnitrate, PETN and nitroglycerine, has no foundations.

Liquid PETN has much in common with nitroglycerine and other nitro esters also with respect to development of disintegration in time. This refers both to the fact that it is a two-phase process, and also to the effect of the degree of filling of reaction vessel by explosive, an increase of which decreases gas formation rate in the first stage and increase it in the second. If this last effect is definitely connected with the achievement of a certain pressure of gasiform products of disintegration and corresponding to a certain critical concentration of them in liquid, then the nature of acceleration in the initial stage is not fixed. Apparently, this acceleration is the result of the course of successive reactions, during which in their first stages less gases will be liberated than in subsequent stages.

Experiments on decomposition of solution of PETN in trotyl show, first, the inaccuracy of the conclusion of a number of preceding investigators concerning the fact that trotyl accelerates the disintegration of PETN. In reality the presence of trotyl even leads to some delay of gas formation, but this effect is small and trotyl can be considered as almost an inert solvent. The absence of a substantial dependence of disintegration rate on concentration shows that main reactions are reactions of first order. This indicates that the kinetic characteristics (E and B) of decomposition of PETN in trotyl solutions are practically the same for its melt, during which B has normal value. In this respect our results differ with the data of A. Robertson [15], who obtained for melt a value of activation energy of 47,000 cal/mole instead of 39,500 cal/mole for solution. This circumstance, possibly, is connected with the fact that Robertson conducted experiments at higher temperatures (160 - 225°), when a noticeable part of the substance increasing with temperature changed into vapors, which, as was shown in this work, are decomposed considerably faster.

Disintegration of PETN at temperatures lower than its melting point differs considerably from disintegration of liquid in the first place, according to the magnitude of the rate of initial stage, which is 40 - 100 times (depending upon temperature) less than for melt or solution. This circumstance is not surprising.

Still Hinshelwood [13] and Farmer [14] in the example of tetryl established that melt is decomposed significantly faster than solid matter. This phenomenon was observed later for a number of explosive and nonexplosive substances [12]. Its causes, however, were not established and that explanation, which Hinshelwood gave, is difficult to bring into quantitative agreement with experimental data. Thus, the difference in disintegration rates of solid and liquid PETN represents a particular case of general phenomenon, as was shown as far back as 1939 - 1940 by K. K. Andreyev and V. P. Maslov, by establishing that the disintegration rate of liquid PETN (at 145°) is not affected by trotyl. This case is more complicated than the one examined by Hinshelwood for tetryl. There decomposition leads to formation of a stable intermediate product (according to Hinshelwood - picric acid), the accumulation of which causes progressive liquefaction of tetryl. The same product catalyzes transformation. During disintegration of PETN liquefaction can occur because of formation of an unstable intermediate product, the concentration of which is small and transition into liquid state of PETN can be only partial. Besides, in the case of PETN gasiform products of disintegration rendered strong accelerating influence and thus acceleration of the latter has a dual nature. In any case the accelerating influence of liquefaction completely explains the observation of former investigators relative to the effect of impurities on the stability of PETN. Thus, the difference in molecular weights naturally explains the observation of Urbanski and collaborators [19] concerning the fact that at equal weight the contents of trinitro compounds have a weaker effect than dinitro, and finally, thanmononitro. In principle L. Avogadro [8] correctly explains the difference in effect of trotyl, pentaerythriteacetate and nitrodiglycol with different solubility of PETN in them. Well-grounded also are his conclusions that with a lowering of temperature of the experiment, decrease in disintegration rate will become less because of a decrease in solubility and that below the eutectic point it is absent. The conclusion corresponds fully to the conclusion of K. K. Andreyev and V. P. Maslov (1940), made by them because of the absence of an effect of trotyl on the disintegration rate of liquid PETN.

From the difference in decomposition rates in liquid and solid states of aggregation it follows, particularly that to guarantee maximum stability of PETN and analogous substances one should seek full purification of products from impurities soluble in them. Just so we must consider possibility of liquefaction also during the use of alloys of PETN. It is true, in this case one should consider that lowering of stability for this reason can be observed only if part of the product changes into liquid state, i. e. during relatively increased temperatures. There are no foundations for expecting, for example, that trotyl will have an effect on the disintegration rate of PETN at room and near room temperatures.

The considerable difference in disintegration rates of solid and liquid substances can serve as a source of error when determining kinetic characteristics of decomposition at temperatures lower than melting point. Let us assume that a product, which we consider pure, contains a small quantity of soluble impurities. If we determine the disintegration rate at relatively low temperature, then all the substance will be in solid state and be decomposed consequently with little speed. Determining the rate near (but below) melting point we will have part of the products in liquid state and the disintegration rate will be greater not only because the temperature is higher, but also because of partial liquefaction of substance. Not considering this last circumstance and calculating activation energy by the usual formula $E = R \cdot \ln \frac{k_2}{k_1} \cdot \frac{T_1 T_2}{T_2 - T}$, we will obtain an oversized value of E, and as a result, B also. We must however, add that if this explanation is correct, then the disintegration rate of solid PETN, free from impurities, at all temperatures is many times less than liquid, and the actual relationship of rates is less than the experiment gave for temperatures, near melting point.

Regardless of the explanation concerning the strong temperature dependence of the rate, from this fact itself, it follows that the disintegration rate of solid PETN at low temperatures is indeed small and much less than for liquid nitro ester, including also solution of PETN.

Everything said about solid PETN refers to the initial stage of disintegration; later, when partial liquefaction of PETN sets in and the accelerating action of gasiform products is developed, the rate increases. This increase is larger than for liquid PETN, where one factor of acceleration acts, and the difference in rates becomes smaller, but still the rate for solid PETN, other conditions being equal, always remains less.

Results of the study of decomposition of PETN in vapor are interesting in the respect that similar to other nitro esters, PETN in this state is characterized by a high disintegration rate, although the difference between liquid and vapor is less than during transition from solid state to liquid; acceleration is absent; there is, apparently, no heterogeneous reaction on the surface of the glass.

Analogy with other nitro esters is observed also with respect to the action of water and oxygen, which, while not appearing to have noticeable effect on initial stage of decomposition, shorten the time period to the onset of acceleration.

All these observations during thermal decomposition of PETN fall in the general diagram of the disintegration of nitro esters, according to which the initial reaction of disintegration is the detachment of NO_2 group. Nitrogen dioxide then oxidizes the radical organically-reducing itself to NO. With this water accumulates and hydrolytic reaction develops. The rate of this reaction abruptly increases after achievement of a definite concentration of acid, formed with hydrolysis and by means of the interaction of NO_2 with water. The concentration of acid and water in liquid phase depends also on their pressure over liquid, which in turn is determined by degree of filling of reaction vessel by the substance. In the presence of acid the rate of hydrolytic reaction is so great, as compared with the rate of the reaction of the first stage, that its onset signifies a strong and sharp rise in rate, which constitutes one of the main peculiarities of disintegration of nitro ester and during suitable conditions can lead to thermal triggering of explosion.

The addition of water to PETN makes possible from the very beginning the course of hydrolytic reaction. Besides, with this reaction will be formed not oxide of nitrogen, but, judging by data for nitroglycerine, - directly nitric acid.

The accelerating action of oxygen one should attribute to the conversion of oxide of nitrogen into dioxide which, on the one hand, accelerates oxidizing reactions, and on the other, promotes an increase in the concentration of acid. The especially strong effect of oxygen is developed during thermal decomposition of nitro esters like nitrocellulose and diglycoldinitrate, whose products of initial stages of disintegration strongly reduce NO_2. As a result of this reduction in the absence of oxygen, disintegration becomes self stabilized, that is its sharp acceleration does not set in at all, at least at increased temperatures (above 100°).

Conclusions

Disintegration of PETN in melt, solution, vapor and solid state was studied by the manometric method. Disintegration rate was the biggest in vapor and smallest in solid state. Melt and solution (in trotyl) are identical in rate of decomposition and occupy an intermediate position, near to other nitro esters (nitroglycerine, nitroglycol). Disintegration in vapor proceeds at a rate, diminishing in time. In liquid and solid states are observed two macrostages of disintegration: a) with a small slightly increasing rate, not accelerated by gasiform products of disintegration and b) characterized by a strong increase of rate in connection with hydrolytic action of formed water, strengthened by acid products of disintegration.

The decomposition rate of solid PETN increases also as a result of its partial liquefaction by products of disintegration. The comparatively high stability of PETN at normal temperatures is caused by the fact that it is in solid state. Trotyl somewhat lowers the decomposition rate of liquid PETN and can accelerate disintegration of solid PETN only in so far, as part of the latter changes into liquid state.

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Chapter 2 Article No. 19

Pages 274 - 280

B. S. Svetlov

19. Thermal Disintegration of Diethylene Glycol Nitrate in the Liquid Phase

From a number of liquid nitro esters the most fully studied with respect to thermal disintegration is nitroglycerine [2], [3], [4], [5]. For it, besides the basic kinetic characteristics, were established the following peculiarities of disintegration: 1) The presence of two kinds of disintegration, one of which is distinguished by a very strong degree of self-acceleration, as a result of which the speed of decomposition can be increased one hundred and more times; 2) The ability to easily and with self-acceleration to interact with added water.

These peculiarities are conditioned by the fact that during disintegration of nitroglycerine in it side by side with other products nitrogen dioxide is accumulated [6], and also nitric and nitrous acids, formed as a result of hydrolysis of nitro esters and interaction of water with oxides of nitrogen. The indicated products also lead to self-accelerating decomposition, developed due to hydrolysis of nitro esters by water, formed as a result of oxidizing reactions. Accumulation of nitrogen peroxide and acids is conditioned, apparently, by the relatively low speeds of their reduction.

Nitroglycol, and also according to the data of B. I. Kaydymov and pentacrytrite-tetranitrate in a fusion or in solution generally exhibit the same regularity of disintegration as that of nitroglycerine.

Thermal disintegration of practically important nitro esters of diethylene glycoldinitrate to the present time has not been studied much. In distinction from nitro esters of the nitroglycerine type diethylene glycoldinitrate is characterized by the presence of an ethereal grouping, and also a relatively small number of nitrate groups, on an atom of carbon in its molecule. It was possible to expect that the indicated circumstance will be reflected on the regularities of decomposition of this nitro ester.

For study of thermal decomposition of diethylene glycoldinitrate manometric methodology was used with a glass manometer of Bourdon, the type allowing to change the degree of filling of the reaction vessel with a substance in wide limits.

Diethylene glycoldinitrate was prepared by the usual method and after thorough washing from acid was preserved in an exsiccator. Temperature of hardening of the obtained nitrate in stable modification constituted 3.1°.

The experiments were conducted[1] in a temperature range of 60 - 150°. In figures 1, 2, 3 are curves of gas formation in time for experiments at 100 - 150° with small and moderate degrees of filling of ampoules ($\delta = 0.0013 - 0.33$)[2]. All curves of change of gas formation in time have a comparitively simple form. The increase of pressure of gaseous products of decomposition takes place monotonously with very small and practically constant acceleration. Speed of gas formation in the process of decomposition increases only by 3 - 4 times as compared with initial speed. In this respect diethylene glycoldinitrate considerably is distinguished from nitroglycerine, the disintegration of which in these conditions is accompanied by very sharp acceleration.

Initial speed of gas formation at thermal decomposition of diethylene glycoldinitrate depends on δ , decreasing with the increase of the latter, simi-

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[1] Students O. I. Sergiyenko and M. P. Koshkin took part in the experiments.

[2] Magnitude δ corresponds to the relation of the volume of nitro esters to the volume of the ampoule in which the experiment was conducted.

lar to how this is observed for nitroglycerine, and other liquid nitro esters.

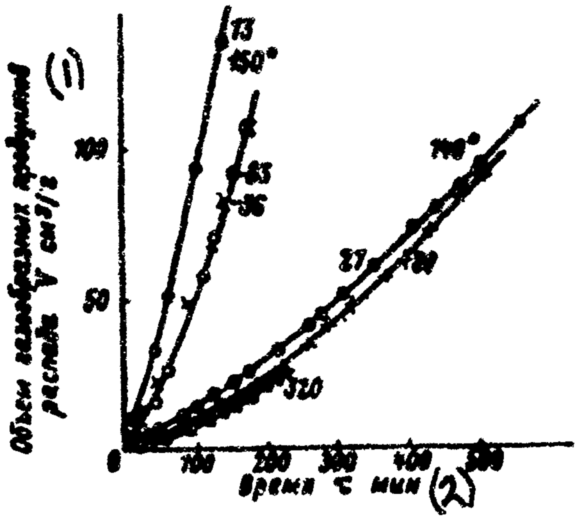

Fig. 1. Thermal decomposition of diethylene glycoldinitrate at 140-150°.
Numbers by curves - degree of filling of ampoule δ . 10^4. 1) Volume of gaseous products of disintegration V cm^3/g; 2) Time τ minutes.

Dependence of initial speed of gas formation on temperature is subordinated by an Arrhenius equation and is represented in fig. 4. Slope of the straight lines on this figure in coordinates $\lg \frac{\Delta p}{\Delta \tau} - \frac{1}{T}$ is approximately identical for different series of experiments, distinguished by degree of filling of reaction vessel with nitro esters, at the time when the absolute values of initial speeds of gas formation change with magnitude δ. Activation energy, calculated for the described experiments, constitutes nearly 42 kilocalories mole, and the logarithm of the pre-exponential multiplier is 16.5. These magnitudes are near to those obtained for disintegration of nitroglycerine in the same conditions. The absolute values of initial speeds of gas formation at disintegration of diethylene glycoldinitrate are approximately 5 times less, than for nitroglycerine and close/ to speeds of gas formation at disintegration of nitroglycol and nitrocellulose [1]. For comparison of these data among themselves in the table are the values of constants of disintegration rate, calculated by an equation for monomolecular reaction on the initial section of gas formation at $\delta \approx 0.01$ (see page 277).

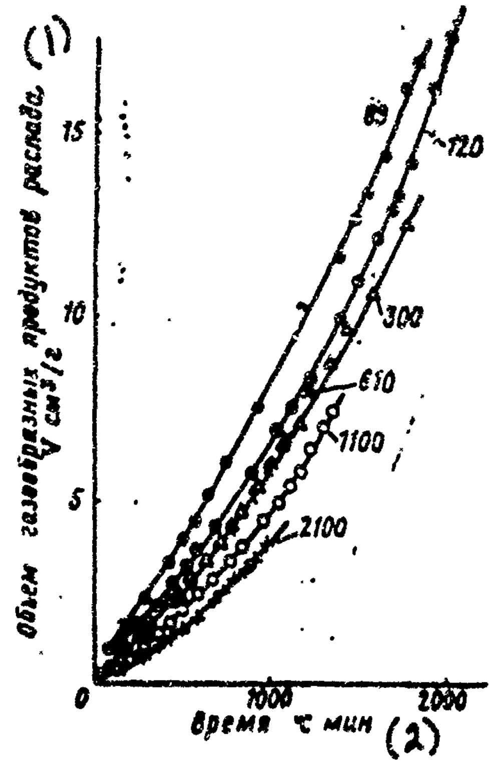

Fig. 2. Thermal decomposition of diethylene glycoldinitrate at 120°.

Numbers by curves - degree of filling of ampoule $\delta \cdot 10^4$. 1) Volume gaseous products of disintegration V cm^3/g; 2) Time τ minutes.

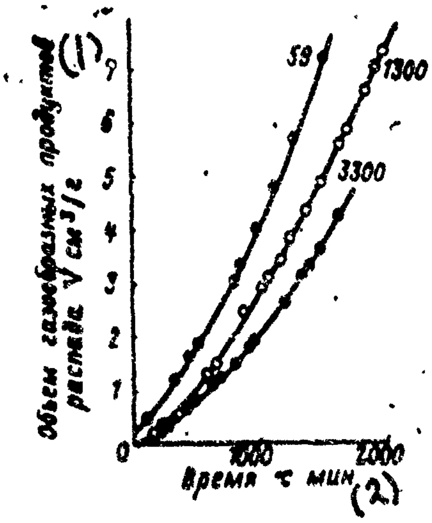

Fig. 3. Thermal decomposition of diethylene glycoldinitrate at 100°.

Numbers by curves - degree of filling of ampoule $\delta \cdot 10^4$. 1) Volume of gaseous products of disintegration V cm^3/g; 2) Time τ minutes.

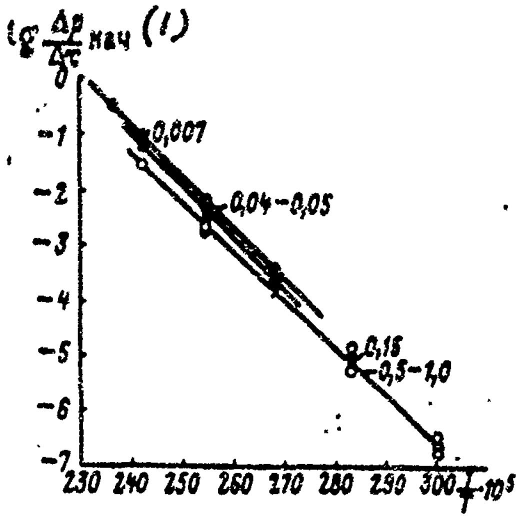

Fig. 4. Influence of temperature on initial speed of gas formation during thermal decomposition of diethylene glycoldinitrate.

Numbers by straight lines - degree of filling of ampoule δ. 1) Initial

Constants of speeds of gas formation during disintegration of certain nitro esters in Sec - 1.

(1) Температура в °C	(2) Диэтиленгликольдинитрат	(3) Нитроцеллюлоза	(4) Нитроглицерин	(5) Нитрогликоль	(6) Тэн в растворе
120	$2 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	$8 \cdot 10^{-7}$	—	$4 \cdot 10^{-7}$
100	$1{,}2 \cdot 10^{-8}$	$1{,}3 \cdot 10^{-8}$	$5 \cdot 10^{-8}$	$1{,}1 \cdot 10^{-8}$	$2 \cdot 10^{-8}$

1) Temperature in °C; 2) Diethylene glycoldinitrate; 3) Nitrocellulose; 4) Nitroglycerine; 5) Nitroglycol; 6) TEN in solution.

Thus, diethylene glycoldinitrate, in spite of the proximity of initial speeds of its disintegration to the disintegration rates of other liquid nitro esters, is distinguished from them by the absence of a stage of sharp acceleration of disintegration.

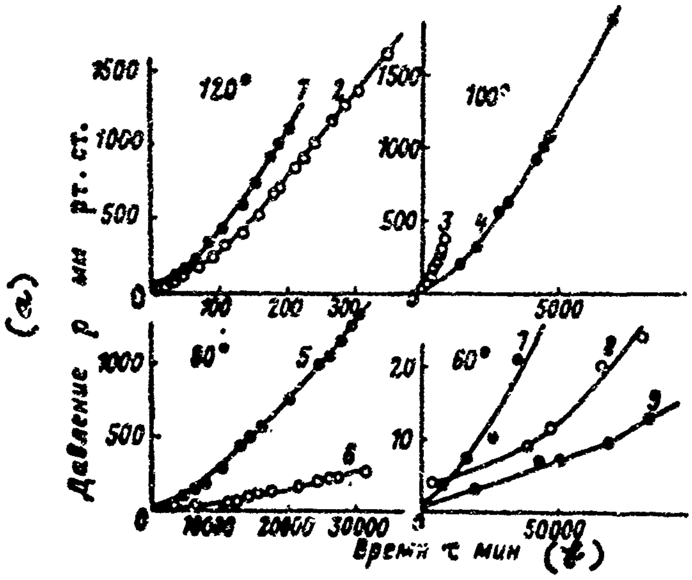

Fig. 5. Thermal decomposition of diethylene glycoldinitrate at a great degree of filling of ampoule.
Degree of filling of ampoule δ : 1-0.95; 2-0.83; 3-0.90; 4-0.60; 5-0.90; 6-0.663; 7-0.90; 8-0.77; 9-0.45. a) Pressure p mm Hg; b) Time τ minutes.

It is known that an increase of degree of filling of the ampoule promotes development of self-accelerated decomposition of such nitro esters, as nitroglycerine, nitroglycol and others, since the approach of the stage of sharp acceleration of disintegration is connected with the active participation in this process of gaseous products of decomposition [2], [3], [4]. Considering this, it was possible to expect that an increase of δ will allow to receive sharper acceleration also during disintegration of diethylene glycoldinitrate.

The experiments were conducted at 60 - 140° and δ from 0.45 to 0.95. Their results are shown in fig. 5. At 140° gas formation was so fast that a kinetic curve could not be taken.

As can be seen from the graphs, decomposition in these conditions proceeds approximately the same way. As at small δ . In beginning of disintegration there is observed certain acceleration by 2 - 3 times, after which a growth of pressure occurs almost in a straight line. Dependence of initial speed of gas formation on temperature also is subordinated by Arrhenius equation. (see fig. 4), and besides the activation energy E constitutes 41 kilocalories mole, i. e. the magnitude, practically equal to that observed for smaller δ .

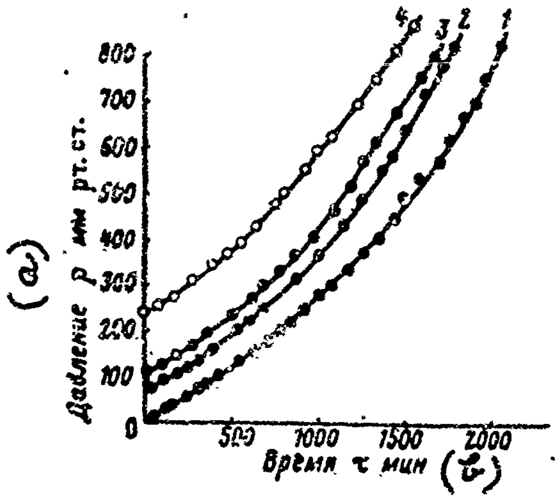

Fig. 6. Thermal decomposition of diethylene glycoldinitrate in the presence of water at 120° and degree of filling of ampoule $\delta = 0.020 - 0.033$.

Contents of water in % by weight: 1 - 0.0; 2 - 0.13; 3 - 0.24; 4 - 0.60. a) Pressure p mm Hq; b) Time τ minute.

In this respect diethylene glycoldinitrate is greatly distinguished from nitroglycerine, for which magnitude E at low temperatures (40 - 100°) and large δ is comparatively small (29 kilocalories mole). In accordance with this, if at 100° decomposition of nitroglycerine proceeds 3 times faster, than diethylene glycoldinitrate, then at 60° the difference becomes significantly larger and reaches 20 ÷ 30 times.

Thus, one of the distinctive peculiarities of disintegration of diethylene glycoldinitrate is the absence in the described conditions of the experiment of that sharp self-acceleration, which characterizes decomposition of other studied liquid nitro esters (nitroglycerine, nitroglycol, TEN fusion).

The experiments conducted, on decomposition of diethylene glycoldinitrate in the presence of water (see fig. 6), indicated another distinctive feature of this nitro ester.

At the time when disintegration of nitroglycerine, nitroglycol, and also in known conditions pentacrythrite tetranitrate in the presence of water is characterized by a section of constant pressures, after which follows a clear depression on curve $p = f(\tau)$ with subsequent acceleration, approaching significantly earlier and more sharply, than during disintegration of a dry substance, gas formation during decomposition of moist diethylene glycoldinitrate proceeds in exactly the same way, as dry. Water does not affect decomposition of this nitro ester both in the beginning, and also on subsequent stages of disintegration. In this respect diethylene glycoldinitrate is similar with nitrocellulose [1].

The third distinctive peculiarity, apparently, stipulating the first two, consists of the fact that in gaseous products of decomposition of diethylene glycoldinitrate nitrogen peroxide is not detected. Visual observation showed the absence of brown color of the gas phase for the duration of all disintegration at its different conditions. For a more reliable estimate special photoelectrocolorim etric experiments[1] were conducted, confirming the results of these observations. Diethylene glycoldinitrate decomposed in the vessel, equipped with, besides a glass manometer, a container of plane-parallel glass. Through the container passed a beam of light, falling on a photocell, which fixed the change of optical density of gaseous products of disintegration. At disintegration of diethylene glycoldinitrate a change of optical density was not observed for the gas phase, which indicates the absence in it of NO_2 in sensitivity frames of a method, which consisted in preliminary calibration of 1 mm Hg of nitrogen peroxide.

In noting the marked peculiarities, it is possible to schematically present decomposition of diethylene glycoldinitrate in the following way.

The primary act of decomposition, as is proposed for nitro esters, is the breakaway of NO_2, which is coordinated with the proximity of initial speeds of

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[1] This methodology was developed by V. P. Shelaputina, to whom the author expresses his gratitude.

gas formation and kinetic disintegration constants of diethylene glycoldinitrate and other nitro esters. The forming nitrogen peroxide is very quickly reduced, apparently. to NO, not being accumulated in any significant quantities, in distinction from that, as this occurs at disintegration of other nitro esters. Reduction occurs not only at interaction of nitrogen peroxide with other products of disintegration of diethylene glycoldinitrate, but, apparently, also at interaction of it with the nitro esters themselves[2].

The leading reaction, determining the kinetic disintegration constants, is the reaction of breakaway of NO_2, as the slower one.

Inasmuch as nitrogen peroxide is not accumulated, then nitric and nitrous acids will not be formed, able to accelerate hydrolytic decomposition of nitro esters. Interaction of nitro esters with water, the presence of large quantities of which in products of disintegration was detected by M. S. Plyasunov, in a neutral medium, as the experiments showed, proceeds with very low speed. Therefore decomposition of diethylene glycoldinitrate is not accelerated in such a degree, as nitroglycerine, although oxidizing reactions occur with comparatively great speed.

What has been said does not mean that decomposition of diethylene glycoldinitrate at all conditions will preserve the described character. The experiments of B. A. Lur'ye on the study of disintegration of this nitro ester in the presence of a number of impurities show that in determined conditions it is possible to observe significant acceleration of decomposition of diethylene glycoldinitrate. The results of these experiments are considered in the following article.

Weak acceleration of gas formation, observed in the experiment, is connected,

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[2] The experiments, conducted by B. A. Lur'ye, show that nitrogen peroxide, added in a quantity of about 1% to diethylene glycoldinitrate, disappears many times faster, than decomposition of the nitrate itself occurs.

apparently, with the passage of sequence reactions, including both the primary breakaway of NO_2 with its reduction, and also deeper disintegration of the compounds forming with this. With this is coordinated, in particular, that fact tha even at comparatively large δ (to 0.13), where is attained by conditions of the experiment only a small degree of disintegration, the composition of gaseous products succeeds to endure definite change. Thus on initial stages the conditional portion of gases condensed at room temperature is 50%, at the time as a measure of development of decomposition it falls noticeably and at a sufficiently great degree of disintegration is lowered to 20 - 30%.

Conclusions

1. The disintegration of diethylene glycoldinitrate in liquid phase in the presence of products of disintegration at 60 - 150° and degree of filling of ampoule with nitro esters 0.001 - 0.9 was studied.

2. Dependence of initial speed of gas formation is subordinated by Arrheni equation, where E = 41 - 42 kilocalories mole and lg B = 16.5 which is very clos to the corresponding constants of decomposition of other nitro esters in liquid phase.

3. In applied conditions of the experiment disintegration of diethylene glycoldinitrate occurs without sharp acceleration, but also is not accelerated by the addition of water.

4. The absence in products of decomposition of diethylene glycoldinitrate of noticeable quantities of nitrogen peroxide can be explained by the fact that oxidizing processes at disintegration occur significantly faster, than primary separation of nitrogen peroxide. This stipulates those peculiarities of disintegration of diethylene glycoldinitrate, which distinguish it from disintegration of nitroglycerine, nitroglycol and TEN.

5. At relatively low temperature (60° and lower) decomposition of diethyle glycoldinitrate occurs ten times slower than nitroglycerine, which in combinatio

with small inclination to self-acceleration stipulates its comparatively high stability.

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Tape No. MT-63-254
Chapter 2 Article 20
Pages 281-295

B. A. Lur'ye and B. S. Svetlov

20. On the Influence of Certain Impurities on Thermal Disintegration of Diethyleneglycol Dinitrate

The thermal decomposition diethyleneglycol dinitrate (DEGDN) without removal of the disintegration products proceeds in known relationship similar to the decomposition of many other polynitro esters. As the initial speeds of gas formation are close, so also is their dependence on temperature, i. e. activation energy. In connection with the fact that the initial stage of disintegration of a nitro ester is, probably the rupture of the $O - NO_2$ bond, this similarity is not surprising.

Development of disintegration of DEGDN occurs, however, without the sharp acceleration of gas formation characteristic for the decomposition of such nitro esters as nitroglycerine (NG), nitroglycol (NGL), PETN, and certain others [3]. This acceleration, as considered in [1], [3], is determined by the hydrolytic decomposition of the nitro ester, self-accelerated because of the formation of acids as a result of the interaction of water with the highest oxide of nitrogen accumulated during the disintegration of these nitro esters [6], [8].

During the thermal decomposition of DEGDN no browning is observed of the gasiform phase, which would attest to the formation of significant quantities of NO_2. This peculiarity hypothetically determines the reducing nature of the nitro ester and products of its disintegration. Therefore we studied the decomposition of DEGDN in the presence of different oxidizers (O_2, NO, NO_2, HNO_3), and also reducing agents ($H_2C_2O_4$).

Another aspect of the investigation consisted in the clarification of those conditions, with which the development of disintegration of DEGDN with sharp self-acceleration is possible.

The decomposition of DEGDN in the presence of the enumerated impurities was studied by the manometric method described earlier [3]. The degree of filling of volume of reactionary vessel with nitro ester ([illegible]) at 120° in the majority of experiments constituted 0.014-0.04 and at 100 and 80°, 0.10-0.13.

The investigated impurity was introduced into the ampule of the glass manometer containing the nitro ester, preliminarily freed from volatile substances by evacuation. Gasiform of highly volatile substances were introduced into the instrument from a vessel intended for their quantitative measurement, with cooling of the ampule of nitro ester by liquid nitrogen.

The oxygen applied was technical, dried in a trap with liquid nitrogen; the oxide of nitrogen was prepared in a Lunge nitrometer, and the dioxide by mixing a known quantity of the oxide nitrogen with a surplus of oxygen with exhaust of the latter with cooling by liquid nitrogen after 1-1.5 hr of interaction; nitric acid was introduced in the form of 98% HNO_3 or its 20% solution in DEGDN, after which, with cooling of the ampule by liquid nitrogen, the air was evacuated from it; oxalic acid was added in the form of a powder and also, depending upon whether the disintegration of the nitro ester was studied in the presence of dilute or concentrated acid, its crystal hydrate or anhydrous crystals were applied.

Dilution of acids by water, if this was required by the conditions of the experiment, was done by transfering its vapor into a cooled ampule.

For determination in the course of the experiment of the content of nitrogen peroxide in the gasiform phase we applied the colorimetric methodology developed in reference to disintegration of nitro esters in the liquid phase by V. P. Shelaputina, whom the authors thank for courteously making possible the setting up of these experiments, and also for help during their completion.

The diagram of the corresponding instrument is shown in Fig. 1. Vessel 1 with plane-parallel optical glasses 2 soldered in it, is connected with glass manometer 3 of the usual type applied for measurement of general pressure. Manometer has ampule 4 for the investigated nitro ester.

After evacuation of air and introduction of the impurity the vessel was placed in thermostat 5, and its ends were tightly secured in seats 6. Then the thermostat was filled by liquid preheated to a determined temperature, after which the mixing and regulated heating were switched on.

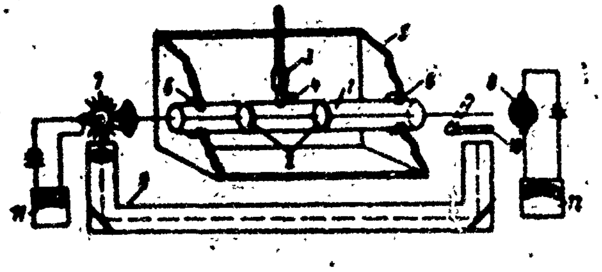

Fig. 1. Diagram of instrument for quantitative determination of nitrogen peroxide in the course of disintegration of nitro ester. 1) Vessel; 2) Plane-parallel optical glasses; 3) Glass manometer; 4) Ampule for nitro ester; 5) Liquid thermostat; 6) Seats for vessel; 7) Source of light; 8) Photoresistance; 9) Control light guide; 10) Mirror; 11) Milliammeter; 12) Microammeter.

Presence of the vessel allowed measurement in the process of the experiment not only of pressure, but also of changes in the optical density of the gaseous phase, which was colored a more or less intense brown color, depending upon the content of nitrogen dioxide. For this, the beam from light source 7 passed through the vessel and was focussed on photoresistance 8. The intensity of light the lamp, working from batteries, was controlled by milliammeter 11. The optical density of the gaseous phase was determined at each given moment by the current intensity in the photoresistance circuit, measured by microammeter 12. For this the vessel was precalibrated with nitrogen peroxide. For the purpose of control of the operational stability of the whole system parallel with removal of results of experiment conducted "control" measurements with help of control light guide 9. With rotation of mirror 10 access of light to photoresistance 8 through the vessel is stopped. In this case light from the source itself falls on the photoresistance through control light guide 9, by passing the vessel. For the difficulty of possible sweating of optical glasses 2 as a result of their cooling by air through the end apertures of the vessel, the ends of the latter were heated by an electrospiral at the suggestion of V. P. Shelaputina.

The accuracy of quantitative measurement of nitrogen peroxide by this method can be judged if one will compare the pressure of NO_2 introduced before the experiment with its quantity measured colorimetrically. The difference between them did not exceed 10%.

Thermal Disintegration of DEGDN in the Presence of Oxygen

Oxygen can change considerably the picture of gas formation during the thermal disintegration of DEGDN. The decomposition of this nitro ester at 120° and sufficiently great pressure of oxygen becomes a two-stage process; this follows from the character of the curves depicted in Fig. 2. The first stage is characterized by small deceleration of gas formation, and also its initial value is higher than during the disintegration of the pure nitro ester. In the beginning of the second stage the speed of gas formation abruptly increases and at large contents of oxygen exceeds by tens of times the maximum speed of gas formation during the disintegration of pure DEGDN.

The influence of oxygen on the decomposition of DEGDN is still more sharply developed at lower temperatures. In Fig. 3 are shown results of experiments at 100°.

With a sufficiently great quantity of oxygen (p_{O2} = 300 - 400 mm Hg) decomposition is once more accompanied by a fast drop in pressure, exceeding by 7 times the rate of gas formation in the disintegration of pure DEGDN.

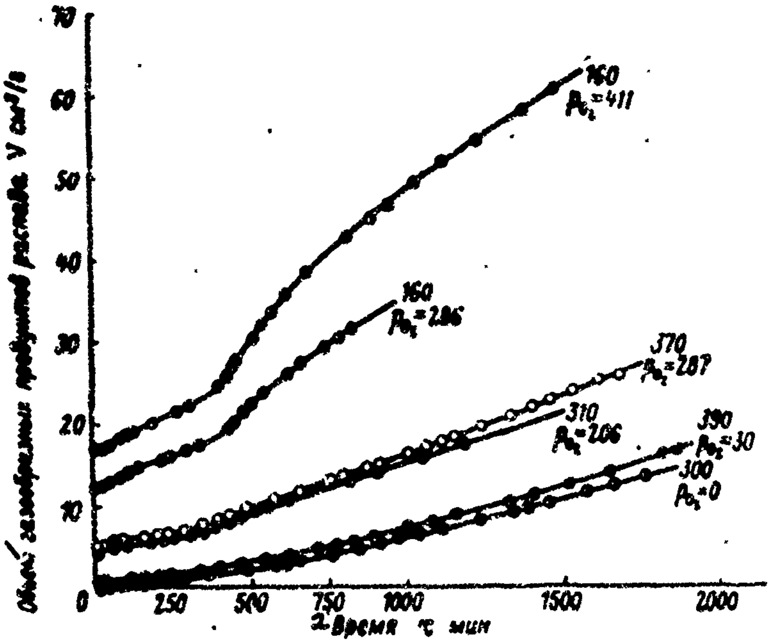

Fig. 2. Influence of oxygen on thermal disintegration of DEGDN at 120°.

Numbers by the curves — degree of filling of the ampule with nitro ester $\delta \cdot 10^4$; p_{O2} — Initial pressure of oxygen, mm Hg, at experimental temperature; 1—Volume of gasiform products of disintegration (v), cm3/g; 2—Time τ min. (Volume of products here and below includes volume of impurties).

Pressure falls by 20-30% from its initial value. After that it starts to grow, at first fast, but then slower, but by 7-8 times faster than for the pure nitro ester. Further disintegration of the nitro ester in the presence of oxygen proceeds also very fast. At 80° the influence of oxygen is in general the same as that at 100°, but the pressure drop proceeds relatively more abruptly. At a content of oxygen corresponding to an initial pressure p_{O2} = 200 mm Hg, the pressure fell approximately by half after 50 hr.

Thus at a definite stage oxygen accelerates the decomposition DEGDN, and the more so, the lower the temperature. The greatest acceleration is observed either in the beginning of the second stage (120°) or after the pressure drop (100-80°); later there occurs a significant drop in the speed of growth of pressure.

It is necessary to note that the disintegration of DEGDN in the presence of oxygen is accompanied by accumulation of nitrogen peroxide in the gaseous phase. The gaseous phase for a certain time after the beginning of the experiment has a light-brown color whose intensity increases, passes through a maximum, and then decreases. At somewhat laters stages of decomposition the gaseous phase becomes again colorless.

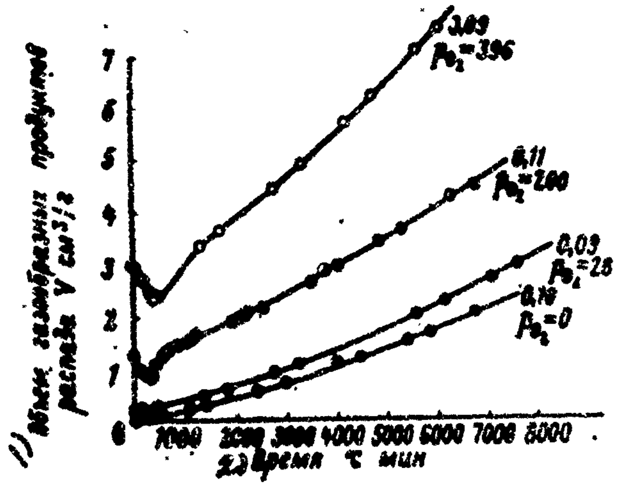

Fig. 3. Influence of oxygen on thermal disintegration of DEGDN at 100°.

Numbers by curves - degree of filling of ampule with nitro ester (δ). p_{O_2} - initial pressure of oxygen, mm Hg, at experimental temperature; 1) Volume of gasiform products of disintegration (V), cm^3/g; 2) Time τ, min.

A quantitative evaluation, conducted passed by colorimetric methodology, showed that at an initial oxygen pressure of 200 mm Hg (120° and = 0.03), the maximum content of NO_2 in the gases (7 vol.%) is attained with a growth in pressure by 1.5 times. In connection with this it was possible to assume that the influence of oxygen on the acceleration of decomposition of the nitro ester is caused by the formation of nitrogen peroxide during the interaction of O_2 with the oxide of nitrogen. However, it is possible that the formation of NO_2 is not the only cause of acceleration of DEGDN decomposition.

Experiments on the heating of initial alchol -- diethyleneglycol -- in the presence of oxygen showed that with this there occurs absorption of oxygen with a significant speed (Fig. 4), and besides there will be formed products possessing properties of peroxides and acids. It is possible that analogous compounds will be formed during the interaction of oxygen and DEGDN and will show a corresponding influence on the decomposition of the latter.

Oxygen affects decomposition of not only DEGDN. According to the data of Samsonov [2] it accelerates the disintegration of nitrocellulose, which in the presence of large quantities of oxygen is decomposed just as nitroglycerine. Decomposition of the latter can proceed faster in the presence of oxygen, especially at the stage of sharp acceleration of this process. Thus, for example, at 100° and [illegible] 0.003, sharp acceleration of decomposition is attained faster (approximately by 2 times) at an intital pressure of oxygen p_{O2} = 200 - 600 mm Hg.

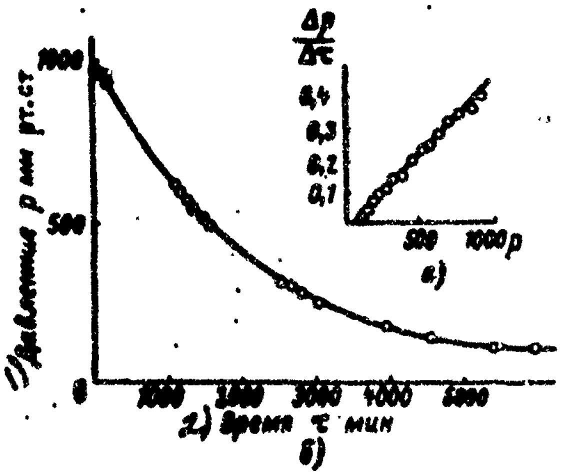

Fig. 4. Interaction of (hyleneglycol with oxygen at 100°.

a - dependence of speed of change of pressure on the magnitude of the latter; b - change of pressure in time. 1) Pressure, p, mm Hg; 2) Time τ, min.

At increased temperature oxygen is able even qualitatively to change the picture of disintegration NG.

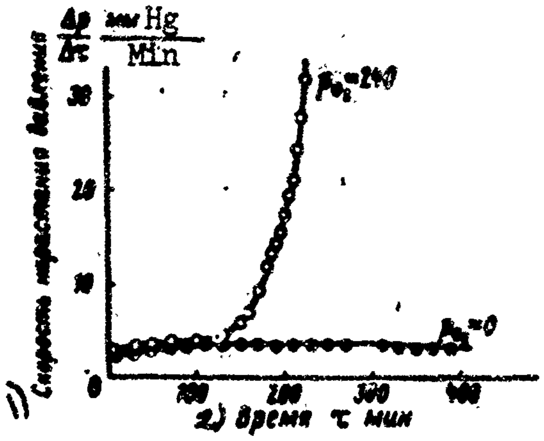

Fig. 5. Influence of oxygen on thermal disintegration of NG at 140° and degree of filling of ampule with nitro ester δ 0.0023.

p_{O2} - initial pressure of oxygen in mm Hg at temperature of experiment. 1) Speed of growth in pressure; 2) Time τ, min.

This at 140° and δ =0.0023, NG is decomposed with an insignificant and practically constant speed, to the time when in presence of oxygen through a certain time, sharp acceleration of decomposition of this nitro ester sets in (see Fig. 5).

Thermal Disintegration of DEGDN in the Presence of Nitrogen Peroxide

In Fig. 6 are shown curves of change of pressure in time for experiments at 120°. These experiments show that gas formation during the thermal decomposition of DEGDN proceeds the faster the more nitrogen peroxide is introduced. At initial p_{NO2} = 120 mm Hg, gas formation occurs practically with the same speed as in the case of pure nitro ester. Increase of initial p_{NO2} to 220-250 mm Hg or, in other words, an increase of the content of nitrogen peroxide, leads to growth of the speed of gas formation by 1.5 - 2 times, and at p_{NO2} = 410 mm Hg -- by 3 times, in comparison with experiments without addition of NO_2.

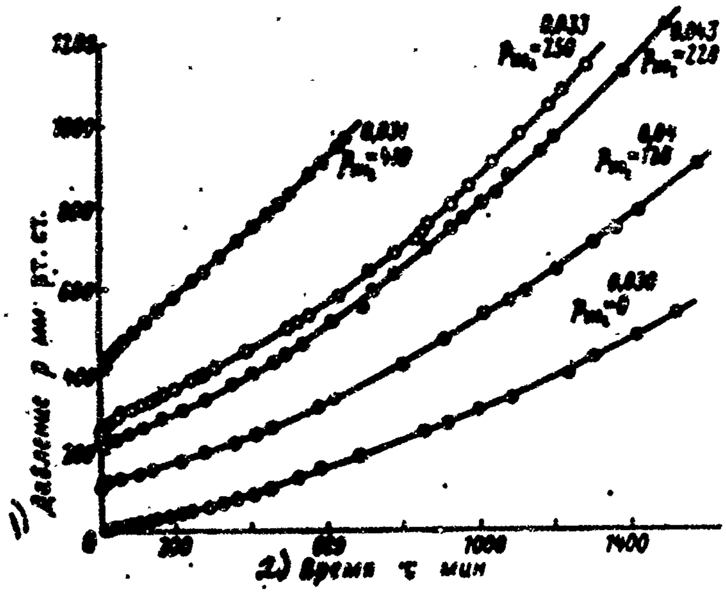

Fig. 6. Influence of nitrogen peroxide on thermal disintegration DEGDN at 120°.

Numbers by curves - degree filling of ampule with nitro ester, δ . p_{NO_2} - initial pressure of nitrogen peroxide in mm Hg at experimental temperature; 1) Pressure, mm of Hg; 2) Time τ, min.

At 100° (Fig. 7) the influence of nitrogen peroxide on the decomposition of DEGDN is in general similar with that which is observed at 120°. The difference consists only in the fact that in the beginning of an experiment with a large content of NO_2 there appears small section of pressure drop (in Fig. 7 it is not covered; see Fig. 9, where this section is shown); further growth in pressure occurs for the duration of a certain time almost linearly, and besides the speed of gas formation at large contents of NO_2 is higher than the speed of decomposition of pure DEGDN by 3 - 10 times. A relatively small quantity of nitrogen peroxide (initial p_{NO_2} = 60 mm Hg) significantly (by 3 times) lowers the speed of gas formation in the first stages of decomposition of the nitro ester in comparison with experiments at large initial p_{NO_2}; further decomposition proceeds with the same speed as for the pure product.

Nitrogen peroxide accelerates disintegration DEGDN especially strongly in the initial stage at 80° (Fig. 8). At $p_{NO2} = 75$ mm Hg the speed of gas formation, calculated as the average for the duration of the first five hours of the experiment, exceeds the speed in experiments with pure DEGDN by 20 times, and $p_{NO2} = 190$ mm Hg, by 200 times. Curves of pressure vs. time in a certain stage of disintegration have a saturable character.

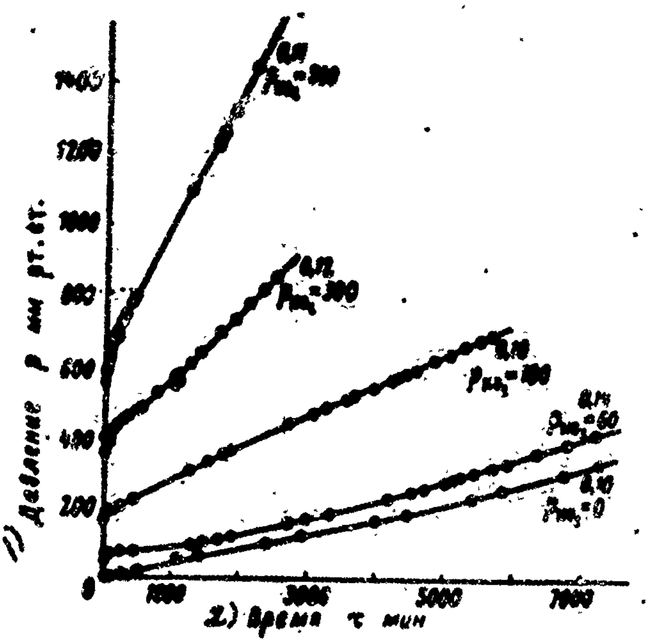

Fig. 7. Influence of nitrogen peroxide on thermal disintegration of DEGDN at 100°.

Numbers by curves - degree of filling of ampule with nitro ester, δ . p_{NO2} - initial pressure of nitrogen peroxide in mm Hg at experimental temperature. 1) Pressure p, mm Hg; 2) Time τ, min.

Visual observation of the color of the gaseous phase shows that during the decomposition of DEGDN in the presence of nitrogen peroxide, the content of the latter does not remain constant, but noticeably decreases, and besides, if the experiment is conducted for a sufficiently long time, then it is possible to reach full bleaching of the gaseous phase.

Considering that NO_2, being supposedly the primary product of disintegration of nitro esters, is absent in gaseous products of the decomposition of DEGDN, it appeared interesting to trace qualitatively the speed of disappearance of nitrogen peroxide in experiments with addition of it.

In Fig. 9 are shown curves of change of pressure of nitrogen dioxide in time in comparison with curves characterizing general pressure. With examination of these curves it is clear that pressure of nitrogen dioxide during practically the period of the whole experiment decreases with a speed, which is greatest in the beginning and is monotonically variable by a complicated law, which on separate sections can be approximated by the equation $\frac{dp}{d\tau} \approx p^n$ where n is larger than unity but less than two.

The decrease in the pressure NO_2 for the duration of certain time occurs considerably faster than the increase in general pressure.

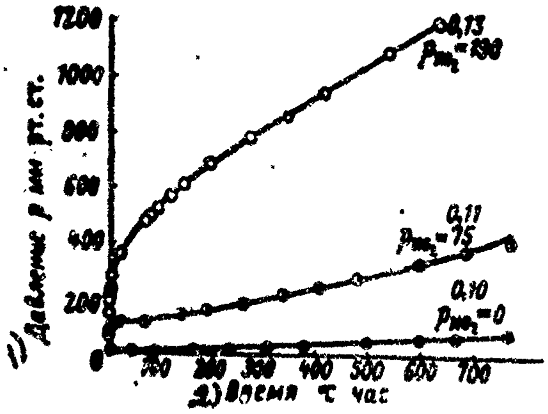

Fig. 8. Influence of nitrogen peroxide on thermal disintegration of DEGDN at 80°.

Numbers by curves - degree of filling of ampule with nitro ester, ε. p_{NO_2} · initial pressure of nitrogen peroxide in mm Hg at experimental temperature. 1) Pressure, p, mm Hg; 2) Time τ, hr.

On the initial section at 140° the speed of the decrease in pressure of NO_2 or, in other words, its disappearance, exceeds the speed of increase in general pressure by more than 2 times, and at 120° — by 5 times. At 100°, and especially at 80°, the speed of disappearance of NO_2 already so much exceeds the speed of general gas formation that on the pressure - time curve a depression is observed whose depth and duration at 80° are larger than at 100°. If with this we compare sections after the pressure drop, then the speed of decrease of NO_2 content exceeds that of general gas formation by 2-5 times.

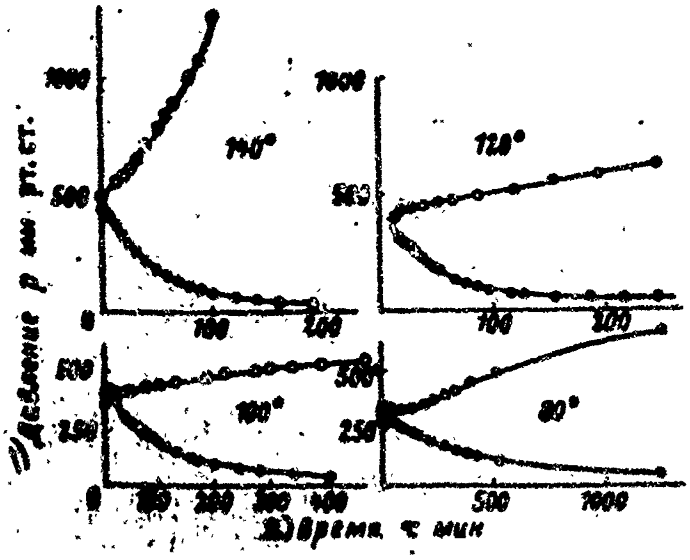

Fig. 9. Change in NO_2 content during decomposition of DEGDN in its presence.

0 - general pressure; ● - NO_2 pressure. 1) Pressure p. mm Hg; 2) Time τ, min.

Thus, the decomposition of DEGDN in the presence of nitrogen peroxide is characterized by the disappearance of the latter from the gaseous phase with a speed exceeding speed of general gas formation.

Thermal Disintegration of DEGDN in Presence of Acids

A basic peculiarity of the decomposition of acidified DEGDN is a sharp growth of gas formation after a small induction period. After passage of a maximum there occurs a fast lowering of the speed of gas formation (Figs. 10, 11, 12, and 13). With this the gaseous phase, colorless in the beginning, is colored the brown color of nitrogen peroxide, vanishing then by the measure of the deceleration of gas formation.

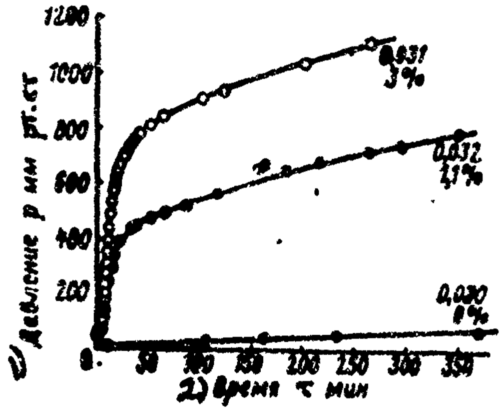

Fig. 10. Thermal disintegration of DEGDN in the presence of concentrated nitric acid at 120°.

Numbers by curves - degree of filling of ampule with nitro ester, δ, and contents of acid in nitro ester in % weight. 1) Pressure p, mm, Hg; 2) Time τ, min.

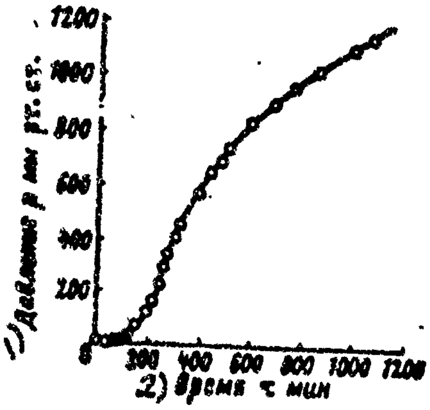

Fig. 11. Thermal disintegration of DEGDN in the presence of concentrated nitric acid at 80° and degree of filling of ampule with nitro ester, δ, of 0.11. (Contents of acid in nitro ester 1.4% weight). 1) Pressure mm Hg; 2) Time τ, min.

The fraction of NO_2 in gaseous products of decomposition is great and attains 90% with an addition of 1.2% oxalic acid. The largest content of nitrogen peroxide is observed near the maximum of speed of gas formation.

In Fig. 10 are shown curves of change of general pressure in time during the decomposition of DEGDN in presence of nitric acid at 120°. The acid shows its own influence on the acceleration of decomposition of nitro ester from the very beginning of the experiment, increasing the initial speed of gas formation as compared with pure DEGDN by 50 to 100 times, depending upon the acid content. Up to the achievement of maximum this speed is increased still by 3 times, after which it falls abruptly.

With lowering of the temperature of the experiment the relative magnitude of the maximum of speed is increased; at the same time the influence of the acid on the initial speed of gas formation changes but little. Thus at 100° ([illegible] ≈ 0.1 [illegible] content of HNO_3 = 1 to 1.5%) the speed in the beginning of the experiment is 30-40 times higher than for the pure nitro ester; at the maximum it increases still by 15 to 30 times. At 80° (Fig. 11) speed after the achievement of the maximum is already 60 times higher than the initial. With this decomposition proceeds with a clearly expressed induction period.

Dilution of the nitric acid added to the nitro ester by water leads to the fact that in the initial stage of decomposition after the achievement of the equilibrium state corresponding to the quantity of added HNO_3 the general pressure (Fig. 12) not only does not grow, but noticeably decreases, attains a minimum and only then begins to increase with significant acceleration. The magnitude of the maximum of the gas formation rate increases with dilution of acid by water.

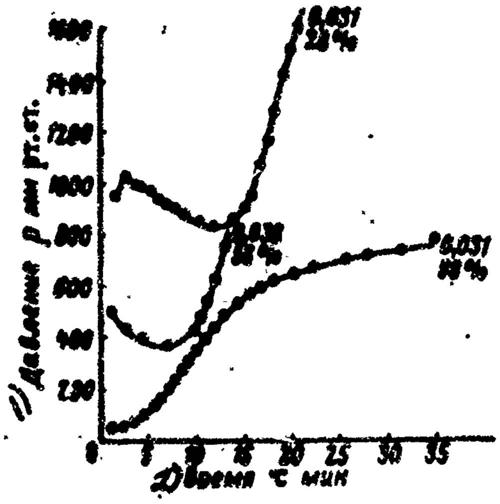

Fig. 12. Thermal disintegration of DEGDN in the presence of nitric acid at different concentrations at 120°.

Numbers by curves -- degree filling of ampule with nitro ester, (•) and concentration of nitric acid in weight %. (Content of acid in nitro ester 3% by weight); 1) Pressure mm Hg; 2) Time τ , min.

In order to exclude the oxidizing action of nitric acid on the nitro ester or on the produc s of its disintegration, we applied oxalic acid, which possesses reducing properties. However, this did not change the general picture of the decomposition of acid DEGDN. In Fig. 13 are shown pressure-time curves for experiments in presence of oxalic acid at different concentrations. These experiments showed that anhydrous acid possesses the greatest ability to accelerate gas formation. It increases the initial speed by more than one hundred times. At the maximum, approaching very fast, speed increases by still two more times[1].

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[1] The presence of maximum of speed is possibly connected with the fact that oxalic acid to the beginning of the experiment is not completely dissolved in the nitro ester. Its dissolution sets in only later, certain small time after the submersion of the instrument in the thermostat.

Application of a solution of oxalic acid containing about 20% water leads to a decrease of the initial and also of the maximum speed of gas formation by 1.5 to 2 times as compared with experiments with anhydrous additions. With the use in experiments of 36% oxalic acid there is observed in the inicial stage a section of decrease in pressure, similar to that in experiments with dilute nitric acid. However, in distinction from these experiments, in the case of dilute oxalic acid gas formation after passage of the pressure minimum proceeds significantly slower than with less dilute or dry acid.

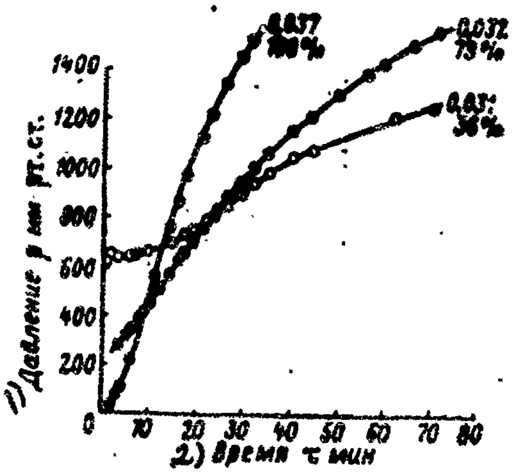

Fig. 13. Thermal disintegration of DEGDN in the presence of oxalic acid at different concentrations at 120°.

Numbers by curves -- degree of filling of ampule with nitro ester, (•) and concentration of oxalic acid in % weight. (Content of acid in nitro ester 3% by weight); 1) Pressure p, mm Hg; 2) Time τ, min.

Thus the decomposition of DEGDN in the presence of the investigated acids proceeds significantly faster and with greater acceleration than in their absence. The main distinction between the action of nitric and oxalic acids is the quantitatively different influence of water on the decomposition of the acid nitro ester. In the case of nitric acid, dilution by water leads to a sharper acceleration of the decomposition of DEGDN than with the concentrated acid; dilute oxalic acid accelerates this process more weakly than does the concentrated acid.

It is necessary to note that nitric acid accelerates the disintegration of DEGDN significant more strongly that it does the decomposition of NG.

Thermal Disintegration of DEGDN in the Presence of Nitric Oxide

As was shown by experiments, nitric oxide can considerably change the character of gas formation especially in the beginning of decomposition of the nitro ester. Thus at 100° (Fig. 14) the addition of nitric oxide in a quantity corresponding to an initial pressure p_{NO} of 108 mm Hg at the experimental temperature leads to a decrease in the general pressure p for a period of approximately 10 hr; the magnitude of this lowering constitutes 20% of the initial pressure. Then the general pressure starts to increase with approximately the same speed as in experiments with pure DEGDN. An increase in the quantity of nitric oxide increases the absolute value of the lowering of general pressure without changing its relative value. The speed of gas formation after passage of the pressure minimum grows somewhat faster at large contents of nitric oxide. An analogous general picture is observed at 120 and 80°. At 120° the lowering of pressure occurs only with contents of nitric oxide corresponding to an initial pressure of 575 mm Hg and more at the experimental temperature. In these conditions the lowering of pressure is small and constitutes only 3% of initial pressure. With a smaller quantity of NO pressure does not fall; its growth in the beginning of decomposition occurs more slowly than in experiments with the pure nitro ester.

At 80° lowering of pressure is observed over a period of 100 hr; it occurs more abruptly and in magnitude constitutes about 30% of the initial pressure of nitric oxide.

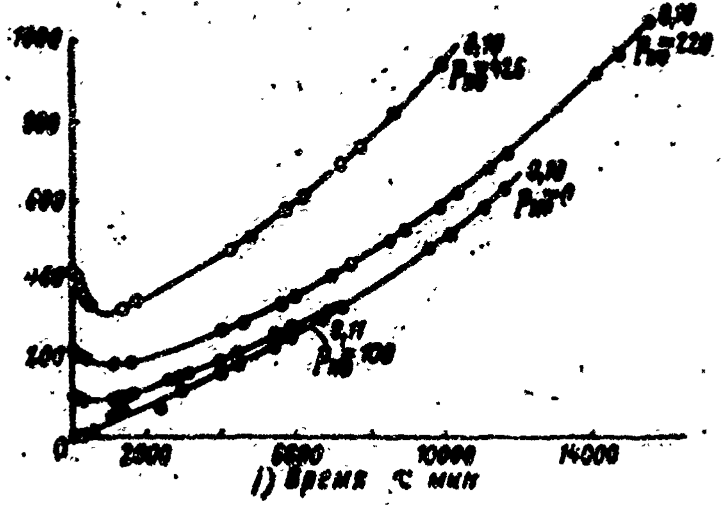

Fig. 14. Influence of nitric oxide on thermal disintegration of DEGDN at 100°.

Numbers by curves — degree of filling of ampule with nitro ester (%), and p_{NO} - initial pressure of nitric oxide in mm Hg at experimental temperature; 1) Time τ, min. (Axis of ordinates — p in mm Hg

Discussion of Results

The results obtained in the experiments show that substances applied as impurities to DEGDN change in this or that degree the picture of gas formation during decomposition of this nitro ester, not only quantitatively but also qualitatively.

The disintegration of DEGDN in the presence of oxygen, the dioxide and oxide of nitrogen, and also strongly diluted acids in certain conditions is characterized first of all by the interaction of the gaseous phase with the liquid, leading to a drop in pressure as a result of binding of gaseous products. If the decrease in pressure with subsequent sharp acceleration during decomposition of DEGDN in the presence of dilute acids can be explained by the course of a hydrolytic reaction with formation of nitric acid highly soluble in the nitro ester, as is assumed for the analogous case in NG [1], [4], then the interaction of oxygen, NO_2 and even of NO with the nitro ester proceeding with a decrease in volume, was not observed earlier and is, apparently, a result of other processes.

Let us consider possible modes of flow of the reaction of DEGDN with the indicated substances.

Comparing the results of experiments on the disintegration of DEGDN in the presence of oxygen with those of experiments on the interaction of the latter with diethyleneglycol, and also, considering the ability of the simple ester to form low-volatile peroxide compounds, it is possible to assume that analogous reactions occur also in the case of DEGDN. The products formed apparently have limited stability during heating, inasmuch as the magnitude of lowering of pressure, characterizing the formation of the indicated compounds strongly depends on temperature. With this is coordinated also the fact that during the analysis of products of interaction of diethyleneglycol with oxygen in a quantity of the latter sufficient to displace the iodine from iodide potassium, constitutes less than 10% of the gas entering in the reaction; the remainder is, apparently, in the form of products of disintegration of peroxides and, in particular, in the form of acid.

The high rate of gas formation during further decomposition DEGDN, observed after passage of the pressure minimum, is probably caused by the whole of the processes, including disintegration of the formed products, and also their participation -- in particular, that of acids -- in the decomposition of the actual nitro ester. Besides this, oxygen can promote the decomposition of DEGDN by oxidizing nitric oxide to the peroxide, which, reacting with water to form the acid, can accelerate the development of hydrolysis of the main product.

The decrease in pressure in the initial period of heating of DEGDN in the presence of NO_2 may be the result of an increase in the solubility of the latter in the decomposed nitro ester or the formation of a comparatively low-volatile compound, analogous to that which is obtained during the interaction of NO_2 with a diethyl ester [5]. Last assumption is indirectly supported by the high speed of interaction of diethyleneglycol with nitrogen peroxide with the formation of low-volatile products.

Inasmuch as nitric oxide is considerably less soluble in DEGDN than NO_2, the decrease in pressure during the disintegration of this nitro ester in the presence NO apparently occurs as a result of the formation of condensed compounds. However, nitric oxide, in distinction from oxygen and NO_2, does not interact with diethyleneglycol. Therefore it is possible to assume that NO_2 detached during the disintegration of molecules of the nitro ester is replaced by nitric oxide, forming the nitrite, as is assumed for ethyl nitrate [7], and NO_2 is bound in a low-volatile compound.

Absence of cases of decrease in pressure in the initial period of the decomposition of DEGDN with addition of nitrogen peroxide and high temperature and also the significant increase in this case in the rate of gas formation in comparison with that in the disintegration of the pure nitro ester show that side by side with the processes assumed above there proceed reactions leading to the formation of products poorly condensed at the experimental temperature. All this, and also the relatively fast disappearance of nitrogen peroxide allows to assume that NO_2 can react directly with DEGDN. Therefore during the decomposition of the pure nitro ester the primary product of the reaction -- nitrogen peroxide is not accumulated; it is formed and immediately enters into further reactions, in contrast to the case of NG, whose disintegration is characterized by accumulation of significant quantities of NO_2.

Nitric acid, apparently, is also capable of the direct oxidation of DEGDN, since gas formation during disintegration of the latter in the presence of this acid proceeds very fast. The acceleration which is observed in this case is probably caused by the sum total of several reactions, which include hydrolysis, accelerated by the measure of dilution of the acid by water formed as a result of the oxidation of the nitro ester.

Curves of gas formation during the disintegration of DEGDN in the presence of nitric and oxalic acids are qualitatively similar; however, the causes of the observed acceleration of this disintegration are different, inasmuch as oxalic acid does not possess oxidizing ability. The accelerating action of oxalic acid on the decomposition of DEGDN can be considered in the light of data on the disintegration of other nitro esters in the presence of acids.

According to the data of B. S. Samsonov, anhydrous sulfuric acid strongly accelerates the disintegration of nitrocellulose from the very beginning of the experiment. According to the data of V. V. Gorbunov the same occurs with NG. This can be explained by the direct interaction of the acid ester with detachment from the latter of nitric acid by an ester exchange reaction. At the same time, G. N. Bespalov showed that dry oxalic acid also very strongly by (tens of times) accelerates the initial stage of decomposition of NG. It is possible that the influence of anhydrous oxalic acid on the disintegration of nitro esters is analogous in nature to the action on them of H_2SO_4. If during the decomposition of DEGDN in presence of oxalic acid there occurs ester exchange the nitric acid formed departs from sphere of reaction, due to its volatility and as a result of oxidation of DEGDN, oxalic acid, and products of reaction. For this reason there occurs fast gas liberation.

Dilution of nitric acid by water leads in the beginning of the experiment to a decrease in pressure after which an increase sets in which is sharper than in the case of anhydrous acid as a result of accelerated gas formation. The dilution of oxalic acid by water, on the other hand, entails delay of disintegration of the nitro ester. Such a distinction can be explained by the fact that water, strongly suppressing the reaction of direct interaction of the nitro ester with oxalic acid, relatively slowly hydrolyzes DEGDN in the presence of this acid.

All the investigated substances, with the exception of nitric oxide, can in certain conditions strongly (by tens and even hundreds of times) accelerate gas formation during the disintegration of DEGDN. However, in distinction from the disintegration of NG, this acceleration is limited by a certain, not very large maximum of speed, approached at comparatively early stages of decomposition and determined therefore not by the expended nitro ester, but by some other causes. The presence of maximum can be compared with the change in color of the gaseous phase, indicating the presence in it of NO_2 in the case of high rates of decomposition. The content of NO_2 in the gaseous phase passes also through a maximum, which is located in time near the maximum of the gas formation rate. Then the content of NO_2 in the gaseous phase decreases by the measure of this drop in rate. All this allows to assume that the subsequent retarding action of substances added to the nitro ester occurs due to the disappearance of these substances. Their disappearance is caused by their interaction with DEGDN and the products of its disintegration. Decomposition of the BEGDN itself, although it generates accelerating substances, does so with a rate less than that of their interaction with the nitro ester. Thus, although the thermal decomposition of DEGDN in the presence of different substances can be strongly accelerated in a definite stage, but in the final analysis there sets in a braking of disintegration, caused by the capability of self-retardation, which is, developed in particular in the case of pure nitro ester in the absence of a stage of sharp acceleration of decomposition. This property considerably distinguishes DEGDN from NG, NGL and certain other nitro esters whose characteristic peculiarity of disintegration is self-accelerated decomposition, developed as a result of the action of products of decomposition.

Conclusion

1. We studied the thermal disintegration of diethyleneglycol dinitrate in the presence of oxygen, NO_2, NO, and nitric and oxalic acids at 80-120°.

2. It was found that liquid DEGDN is able at increased temperatures, to interact with oxygen, NO_2, and NO of the reaction proceeds with a decrease in the volume of these gases.

Binding of oxygen and nitrogen peroxide was established also for DEGDN itself.

3. It was shown that concentrated nitric and oxalic acid accelerate the decomposition of DEGDN by tens and even hundreds of times. Dilution of nitric acid strengthens the acceleration of gas generation, while in case of oxalic acid dilution retards decomposition.

4. The sharp acceleration observed during the disintegration of DEGDN in the presence of certain substances is accompanied by accumulation of NO_2, and is changed after passage of the disintegration rate through a maximum by retardation of gas formation and gradual disappearance of nitrogen peroxide.

5. The data obtained are considered in the light of the assumption of the capacity of DEGDN for self-retardation of decomposition.

6. An assumption was made about the direct interaction of diethylenglycol dinitrate with oxalic acid.

In conclusion authors consider it their pleasant duty to express deep gratitude to K. K. Andreyev for his valuable remarks made during his examination of the manuscript of the article.

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Pages 296 - 309 Article No. 21

B. N. Kondrikov

21. Thermal Decomposition of Dinitrate of Ethylene Glycol and Trinitrite of Glycerine

Explanation of the mechanism of thermal decompositon of nitro esters is essentially hampered by the complexity of this process, stipulated, in particular, by the fact that one of the primary products of disintegration - nitrogen dioxide - is an energy oxidizer, easily interacting with other products of decomposition, and often with the nitro esters themselves. The role of processes of oxidation can be significantly decreased, if during the study of high-temperature transformations we cross from esters of nitric to esters of nitrous acid, the mechanism of disintegration of which, in view of the likeness of chemical structure of these compounds, is similar with the mechanism of disintegration of nitro esters, but as a rule, includes detachment not of dioxide, but oxide of nitrogen - an oxidizer incomparable more weaker. Therefore for the duration here already for more than two decades the investigation of the mechanism of thermal disintegration of nitro esters is inseparably connected with the study of disintegration of organic nitrites. However until very recently investigations of thermal disintegration of esters of nitrous acid were limited basically to mononitrites of monatomic alcohols; polynitrites - the most interesting compounds, in view of their large kinship with widely applied polynitrates - were almost not investigated. This work represents one of the first attempts of a study of thermal decomposition of polynitrites of polyatomic alcohols.

Thermal Disintegration of Esters of Nitrous Acid (survey)

The first systematic investigations of thermal decomposition of esters of nitrous acids were undertaken by Steacie with collaborators in Canada [46] - [55]. The kinetics of decomposition of methyl - [46], [50], [52], ethyl- [47], [54], n - propyl - [48], [54], isopropyl - [49] and n - butylinitrites [51] was studied by namometric method at 170 - 240° and pressure 0.005 — 50 cm Hg (for methylnitrite - up to 3000 cm Hg). It turned out that disintegration of these compounds basically is homogeneous, and the growth of pressure is subordinated to the law of reaction of first order. The relation of pressure of final gaseous products of disintegation to initial pressure of nitrite vapors depends little on concentration and temperature and changes from 1.6 for n-butylnitrite to 2.0 for n - propyl - and isopropylnitrites.

Gaseous products at room temperature contain 80 - 98% NO, 1-10% CO and small quantities of other gases, the nature of which was not explained. In products, condensed at room temperature, aldehydes and alcohols were detected. Activation energy of disintegration for all members of the series turned out to be almost identical and close to 37 kilocalories mole.

On the basis of results of the investigation, Steacie concluded that thermal disintegration of alkylmononitrites represents a simple monomolecular reaction

$$RCH_2ONO \rightarrow \frac{1}{2} RCH_2OH + \frac{1}{2} RCHO + NO \qquad (1)$$

the speed of which is determined by the speed of breaking the bond of RCH_2O--NO

$$RCH_2O-NO \rightarrow RCH_2O \cdot + NO \qquad (2)$$

and activation energy corresponds to the energy of breaking of this bond. The mechanism of reactions, following the break of the bond O - NO, was offered by Rice [44] on the basis of certain indirect data, obtained by him during the study of thermal disintegration of ethylnitrite at 400 - 500°. This mechanism included the following main reactions:[1]

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[1] It was assumed that at small pressures these reactions are also possible:

$$CH_3CH_2O \cdot \rightarrow CH_3 \cdot + CH_2O$$

$$CH_3 \cdot + CH_3CH_2ONO \rightarrow CH_4 + CH_3CHONO$$

The first of them - the main way of disintegration of etoxyl - at present is quite reliably well-grounded experimentally. The second recently was rejected

$$CH_3CH_2O\cdot + CH_3CH_2ONO \rightarrow CH_3CH_2OH + CH_3\dot{C}HONO \qquad (3)$$

$$CH_3\dot{C}HONO \rightarrow CH_3CHO + NO \qquad (4)$$

In spite of the fact that any direct proofs of the existence of reactions (3) and (4) Rice was unable to obtain, this mechanism for nearly two decades was considered to be conventional and was wide-spread not only for disintegration of all remaining esters of nitrous acid both in gas, so also in liquid phase [31] but also for disintegration of alkylnitrates [41].

It is important to note that inasmuch as disintegration of nitrites - this is a reaction of first order, the speed of reverse stage of reaction (2)

$$RCH_2O\cdot + NO \rightarrow RCH_2ONO$$

(i.e. ordinary interaction of nitrogen oxide with radical) with such a mechanism should be significantly less than the speed of reaction (3).[2]

[FOOTNOTE CONTINUED FROM PROCEDING PAGE]
as the result of study of the interaction of methylnitrite with products of decomposition of tert-butylperoxide [30]. In work [30] was offered another reaction of the interaction of methyl with nitrite

$$CH_3\cdot + CH_3ONO \rightarrow CH_3NO + CH_3O\cdot$$

used also by P. Gray for interpretation of data on disintegration tert-butylnitrite [29].

[2] Actually, having designated the constant speeds of reaction by the letter k with an index, corresponding to the number of the equation of the reaction, we obtain (in a usual assumption on the stability of etoxyl concentration)

$$-\frac{d\ln[C_2H_5CNO]}{d\tau} = k_2 + \frac{k_2k_3[C_2H_5CNO]}{k_5[NO] + k_3[C_2H_5ONO]},$$

$$\text{при } k_5[NO] \ll k_3[C_2H_5ONO]$$

this is an equation of reaction of the first order.

Direct experimental check of the validity of this conclusion was undertaken by Levy [34], studying with the help of an infrared spectrometer the reaction of ethyl peroxide in the presence of nitrogen oxide and ethylnitrite at 181° and pressure on the order of several cm Hg. With this temperature the desintegration rate of peroxide is very great, and ethylnitrite for the duration of several minutes should have been decomposed by reaction (3). However not the smallest traces of decomposition were detected. At the same time the speed of reaction (5) was very significant: after 1 -- 2 minutes approximately 20%, and after 4 - 6 minutes - nearly 60% peroxide in the presence of NO changed to ethylnitrite.[1]

The Rice mechanism, thus, turned out to be unsound at least for that area of conditions, for which the main part of experimental data is obtained on disintegration of nitrites and nitrates.

Another mechanism was offered by Levy. The experimental base of this mechanism was the investigation of thermal disintegration of ethylnitrite, conducted by him with help of an infrared spectrometer [37]. In products of disintegration at 160 - 200° were detected acetaldehyde (with yield of 60 - 90% in reference to ethylnitrite), nitrous oxide (20 - 25%), and also small quantities of ethyl alcohol and prussic acids. The speed of disappearance of ethylnitrite was subordinated to the law of reaction of the first order. With the addition of NO the disintegration rate almost did not change, the yield of acetaldehyde was increased to 100%, and N_2O - to 50%. Addition of acetaldehyde led to an increase of the disintegration rate, a decrease of yield of N_2O and certain growth of the quantity of HCN in products of decomposition. The mechanism, offered for explanation of these results, included the following main reactions:

$$CH_3CH_2ONO \underset{k_1}{\overset{k}{\rightleftarrows}} CH_3CH_2O\cdot + NO \qquad (6)$$

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[1] An analogous phenomenon was observed later by Hinshelwood with collaborators [22], detecting that tert-butyl peroxide at 160° in the presence of NO almost quantitatively transforms into tert-butylnitrite.

$$CH_3CH_2O\cdot + NO \xrightarrow[k_4]{} CH_3CHO + NOH \qquad (7)$$

$$CH_3CH_2O\cdot \xrightarrow{k_3} CH_3\cdot + CH_2O^1 \qquad (8)$$

$$2NOH \rightarrow N_2O + H_2O \qquad (9)$$

$$CH_3CH_2O\cdot + CH_3CHO \rightarrow CH_3CH_2OH + \underset{\displaystyle CH_3\cdot + CO}{\underset{\downarrow}{CH_3CO\cdot}} \qquad (10)$$

Consideration of reactions (6) and (7), determining disintegration rate in usual conditions and expecially with the addition of NO, leads to a kinetic equation of reaction of the first order

$$-\frac{d\ln[C_2H_5ONO]}{d\tau} = \frac{k_1k_2}{k_1+k_3} = K,$$

from which, in particular, it follows that activation energy of breaking the bond O - NO in ethylinitrite is a less experimentally determined magnitude (see Table 3 on page 326) on the activation energy of the reaction (7), apparently, by several kilocalories mole.

Later this mechanism was wide-spread in other alkylmononitrites [38], and also with success was used for interpretation of the results obtained by Pollard and his collaborators [42], [43], of the investigation of thermal decomposition of ethylnitrate [10].

In distinction from decomposition of alkylmononitrites, thermal disintegration of polynitrites - this is an area almost completely not investigated. Only quite recently in literature appeared data about thermal decomposition of dinitrites of several glycols at temperatures of approximately 300° [32], [33].

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[1] At 160 - 200° for constants of speed of reactions (7), (8) and reverse stage of reaction (6) following relationships are fulfilled: $k_1 \geq k_2 \gg k_4$. As the results of certain works [33] show at an increase of temperature to 300° the speed of reaction (8) considerably is increased ans approaches the speed of reaction (7).

It is interesting that also for all investigated dinitrites the first stage of disintegration, apparently, is the breaking of the bond O - NO with the formation of a hydroxyradical and NO. The further fate of the hydroxyradical depends on its structure. In decomposition of some dinitrites (propane - 1.2 -, butane - 2.3 - and 1.4 -, hexane - 2.5 - and certain others) the radical is disintegrated or is regroupded, separating NO. Radicals of other dinitrates (propane - 1.3 -, butane - 1.3 -, pentane - 2.4 - and 1.5 - and 2.5 - dimethylhexane - 2.5 -) yield upon disintegration not nitrogen oxide, but nitrogen peroxide, significant quantities of which (together with products of oxidation by nitrogen peroxide of organic substances) were detected in products of the reaction.

It was established that at decomposition of dinitrites close to 300° reactions of type (7), (10) and others do not play any role so clearly developed in disintegration of nononitrites close to 200°. Inasmuch as in a given case there were other conditions of conducting the experiments and the chemical structure of the investigated substances to answer the question about the causes of distinctions in the mechanism of disintegration the authors, naturally, were not able.

Results of these works were used for interpretation of data, obtained during the study of disintegration of nitrocellulose upon burning it in a vacuum [57].

In spite of the fact that in these works, conducted almost simultaneously with our works, was carried out a significant volume of research or disintegration of dinitrites of polyatomic alcohols, a whole series of questions remained untouched. First of all was not completely studied the disintegration of polynitrites at lower (100 - 200°) temperatures, with which was obtained in time a great deal of data requiring interpretation on decomposition of polynitrates. Kinetic investigations of the disintegration of polynitrites practically nonexistant. There was no information about decomposition of the most interesting of them - dinitrite of the simplest polyatomic alcohol - ethylene glycol (as

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strange as it may seem, American investigators having obtained and studies disintegration of more than ten dinitrites do not mention one work about it) and an analog of nitroglycerine - glycerintrinitrite.

In this article are presented the main results of investigations conducted by us of the kinetics and mechanism of thermal disintegration of dinitrite of ethylene glycol and trinitrite of glycerine [9], [10], [5].

Thermal Decomposition of Dinitrite of Ethylene Glycol

Obtaining Dinitrite of Ethylene Glycol

Dinitrite of ethylene glycol was obtained by two methods. By the first of them [21] a solution of glycerintrinitrite in ethylene glycol was heated in a distillation bulb to 100 - 105° and distilled the glycoldinitrite formed by the usual exchange reaction. Trinitrite of glycerine was preliminary prepared [39] by prolonged passage of N_2O_3 through glycerine, dried and sublimated in a current of air at 60 - 100°.

This awkward, inconvenient method later was replaced by obtaining dinitrite of ethylene glycol, analogous to nitrites of other monatomic and diatomic alcohols [6], [32] esterifications of glycol by an aqueous solution of nitrous acid. To an aqueous solution f two equivalents of ethylene glycol and nearly three of sodium nitrite cooled by a mixture of ice and salt during intense mixing was added in drops two equivalents of diluted hydrochloric acid.

The temperature of the mass was not raised above minus 2°. Immediately after termination of pouring the dinitrite was separated and processed by anhydrous soda. Then it was dried by sodium sulfate and sublimated under atmospheric (at a temperature of nearly 96°) and under lowered pressure. The mobile yellow liquid obtained in this manner with characteristic odor was liberated from gases and in a vacuum was transferred to soldered ampoules. Elementary alalysis of it gave the following results.

Found %: C 19.78; 19.97; H 3.60; 3.50; N 23.15; 23.20.

Calculated for $C_2H_4O_4N_2$%: C 20.00; H 3.36; N 23.33.

Index of refraction $n_D^{18.5}$ =1,3884.

The molecular weight, determined by manometric method is 120 ± 0.6. Heat of evaporation, calculated from the dependence of vapor pressure on temperature in the range 16 - 100° on the slope of the straight line in coordinates lg p - 1/T (see Fig. 1), is equal to 8.8 kilocalories mole.

Methodology of Experiment

The kinetics of disintegration in gas phase was studied by measurement of pressure in a static system by a glass manometer of the Bourdon type at 120 - 190° and initial pressure 50 - 1000 mm Hg.

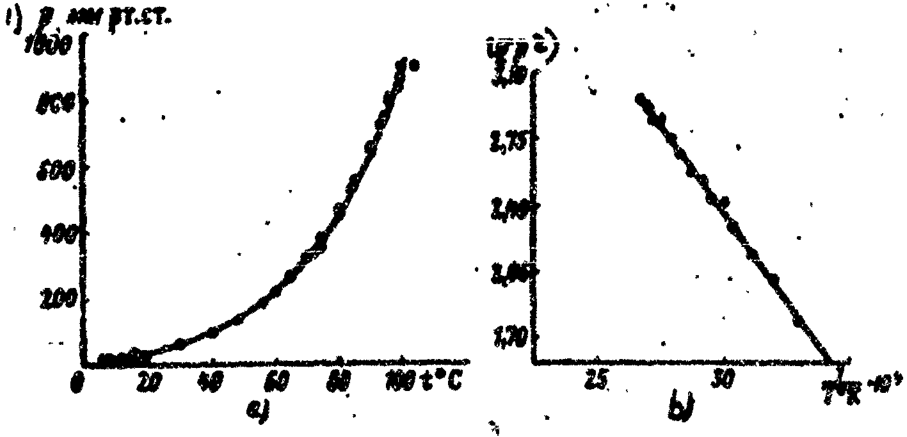

Fig. 1. Dependence of elasticity of vapors of dinitrite of ethylene glycol on temperature.
a - in coordinates p - t°, b - in coordinates log p - $\frac{1}{T}$.
1) p mm Hg; 2) log p.

For introduction of dinitrite and additions into the reactionary vessel was used a vacuum installation of the usual type. An ampoule with dinitrite was placed in a sealed ampoule opener (Fig. 2), the latter was joined to the installation and, upon pumping the system to residual pressure 10^{-2} - 10^{-4} mm Hg, the tip of ampoule was broken by a turn of the cock of the opener.

With storage even in sealed ampoules and in cold dinitrite noticeable is decomposed, therefore after opening the ampoule easily-volatile products of disintegration are removed by prolonged evacuation, then part of the nitrite is transferred into a vacuum in a reaction vessel, cooling the latter with liquid nitrogen, the vessel was heated to room temperature and again the dinitrite was evacuated for removal of remainders of easily-volatile impurities.

The reaction vessel prepared for carrying out the experiment was unsealed and, having determined on the pressure of vapors at 100° the quantity of nitrite in the vessel, it was placed in a liquid thermostat, the temperature of which was maintained constant within the limits ± 0.2°. Time of heating of the substance to the temperature of the thermostat usually did not exceed 0.5 minutes.

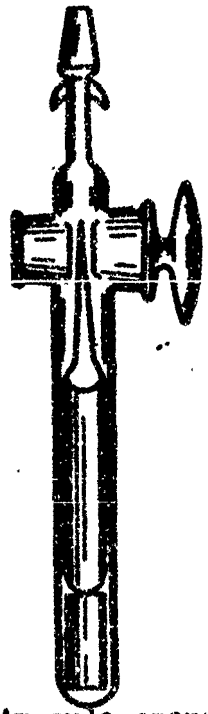

Fig. 2. Ampoule opener.

The final gaseous products of disintegration in the beginning were analyzed by a method, which includes separation from the mixture by means of deep cooling of two fractions: NO, Co and N_2 - in the first (cooling to minus 165°) and N_2O and CO_2 - in the second (minus 100°). NO was absorbed by an acidified solution of $FeSO_4$, CO_2 - 60% solution of KOH, and the contents N_2 and N_2O in separate fractions were determined by the difference.

A method was also used, by which carbon dioxide, and after it, nitrogen oxide with a surplus of oxygen was absorbed by a 60% solution of KOH, nitrous oxide was burned with hydrogen (and besides a little CO was oxidized by the oxide to CO_2), and carbon monoxide - with oxygen on a heated platinum spiral. The formed carbon dioxide was absorbed by the alkali.

Both methods were checked in artificial mixtures; the error did not exceed 1 - 1.5% abs.

Results of Experiments

Influence of Initial Concentration

Manometric curves, obtained at 170° and different initial pressures of blycoldinitrite vapors, are shown in Fig. 3 - 5. The main peculiarity of decomposition of blycoldinitrite, characterized by these curves, consists of the fact that at sufficient high (above 150 mm[1]) initial pressure it has a clearly expressed diphase character, and besides on the first stage the disintegration rate is lowered at first sharply, and then more slowly, on the second - increases, passes through the maximum and quickly decreases to zero.

At small initial pressures the speed of gas formation continuously decreases in time, the kinetic curves have the usual form (at 180° and initial pressure of approximately 70 mm deceleration of disintegration in time occurs according to the law, close to monomolecular - see Fig. 8, b).

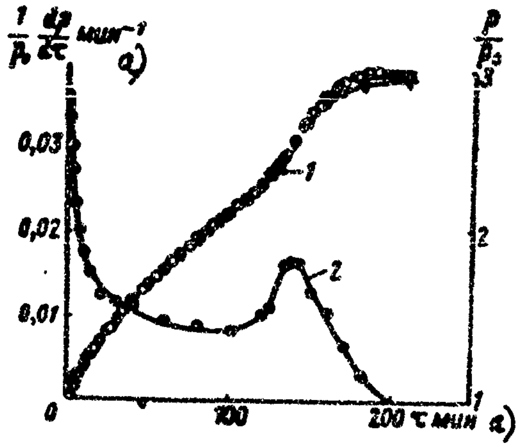

Fig. 3. Kinetics of gas formation at disintegration of glycoldinitrite at 170°.
p_V: 0 - 248, ▲ - 248, + - 251 mm Hg 1 - in coordinates $p/p_v - \tau$;
2 - in coordinates $w - \tau$ (w - speed of increase of pressure). a) minutes.

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[1] All concentrations of gaseous products here and further are expressed in mm Hg at the temperature of the experiment.

Initial speed of gas formation[1] does not depend on concentration of dinitrite.

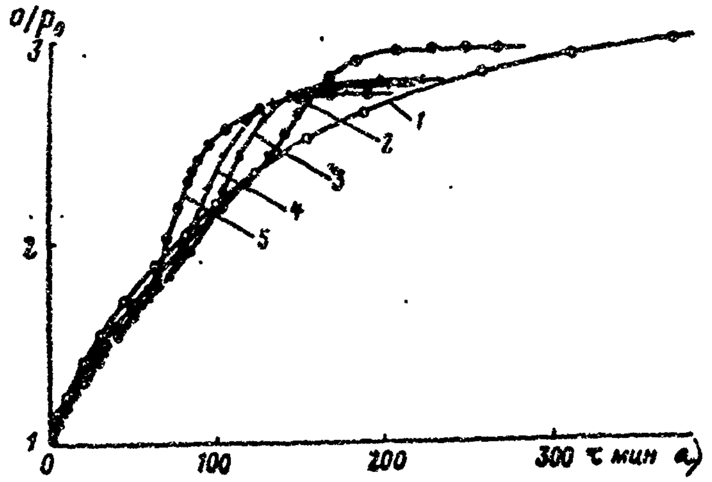

Fig. 4. Influence of initial concentration on decomposition of glycoldinitrite at 170°.
p_0: 1 - 76; 2 - 221; 3 - 320; 4 - 405; 5 - 659 mm Hg
a) minutes.

However on subsequent stages of the first stage of disintegration such a dependence is detected, and namely: in the same moment of time (or at the same relative increase of pressure) in various experiments the speed is lower, the higher the initial concentration of dinitrite (Fig. 5).

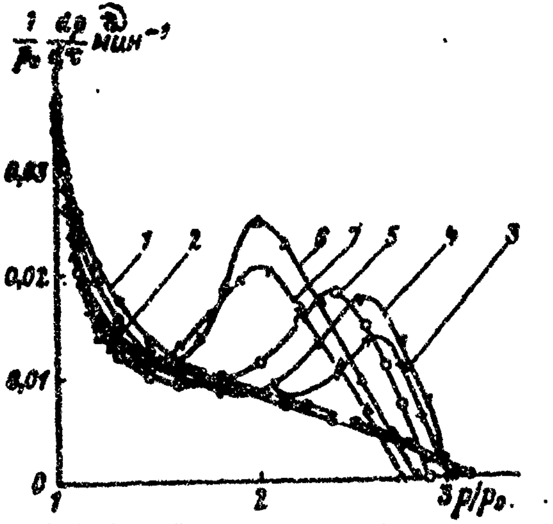

Fig. 5. Influence of initial concentration on speed of gas formation in decomposition of glycoldinitrite at 170°.
p_0: 1 - 76; 2 - 115; 3 - 221; 4 - 276; 5 - 320; 6 - 659; 7 - 920 mm
a) minutes.

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[1] Here and in the future it is a question on speed of growth of pressure, referred to initial concentration of dinitrite $\frac{dp}{d\tau} \cdot \frac{1}{p_0}$, w minutes $^{-1}$.

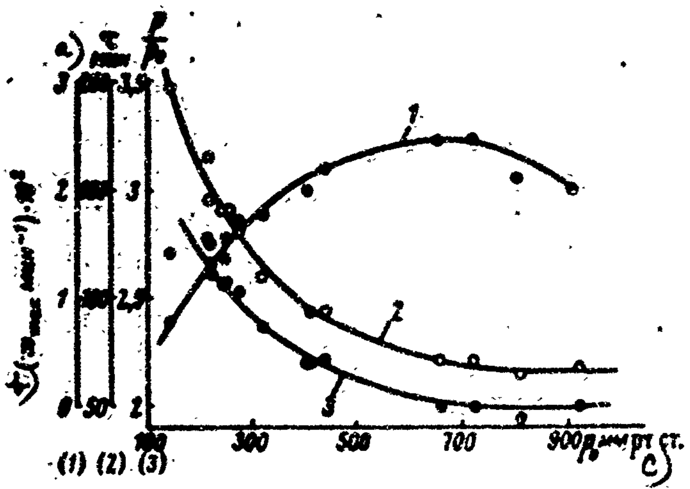

Fig. 6. Dependence of speed on maximum (w_{max}), time of its achievement (τ) and pressure, with which it is attained (p), on initial concentration of glycodinitrite vapors (p_0).
In coordinates: $1 - w_{max} - p_0$; $2 - \tau - p_0$; $3 - \frac{p}{p_0} - p_0$.

a) minutes; b) (w_{max} Min^{-1}) · 10^2; c) P_0 mm Hg.

This influence of concentration is fully defined, but small: at increase of initial pressure from 100 to 400 mm speed of gas formation on average steps of first stage of disintegration decreases 1.2 - 1.4 times, increase of p_0 above 400 mm does not evoke further lowering of speed.

Maximum speed of gas formation at an increase of initial pressure to 600 - 800 mm increases, and then is somewhat lowered. Time of achievement of maximum and pressure, with which it is attained, decrease (see Fig. 6).

Concentration of dinitrite in a determined way influences also the composition of final products of disintegration that is developed, in particular, in the change at increase of initial pressure of the quantity of products, not condensed at various temperatures (see Fig. 7).

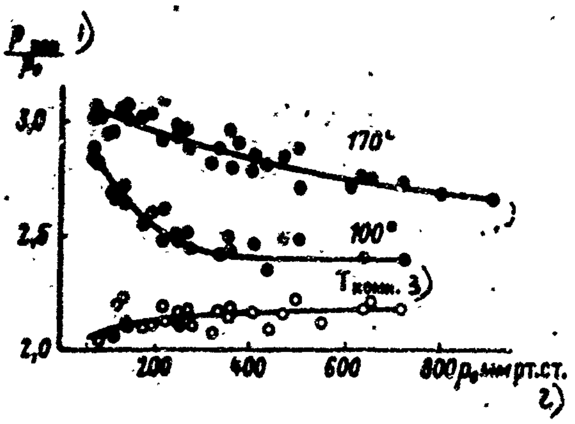

Fig. 7.1 Dependence of quantity of final products of disintegration not condensed at different temperatures, on initial pressure.

1) $\frac{P_{con}}{P_o}$; 2) P_o mm Hg; 3) T_{Room}.

Time of decomposition at an increase of initial pressure is considerably reduced. At 70 - 100 mm it constitutes, at least, 450 - 500, at 140 - 150 mm - 250 - 300, at 200 mm and the higher pressure - 150 - 200 minutes.

Influence of Temperature

At an increase of temperature the influence of concentration on speed of both the first, and also the second stages of disintegration considerably decreases. From Fig. 9 it is clear that at 190° an increase of initial pressure from 140 to 300 mm does not change the speed and does not allow to detect a diphase character of decomposition. The role of the stage of disintegration at an increase of temperature significantly is lowered, and the relation of initial speed to speed on the maximum increases: at 170° and initial pressure 276 mm (Fig. 5) it equals 1.8 and at 180° and 299 mm (Fig. 8) - 3.1.

The initial speed of gas formation at increase of temperature grows. At 170° it constitutes $5.8 \cdot 10^{-4}$, at 180° - $15 \cdot 10^{-4}$, at 190° - $33.3 \cdot 10^{-4}$ sec^{-1}. Activation energy of disintegration of dinitrite, calculated by these speeds, is equal to 35.6 kilocalories mole.

Noticeably increased at increase of temperature is the volume of gaseous final products of disintegration (at p_o = 300 - 400 mm and 170° it equals 2.9

moles per mole of nitrite, at 190° - 3.2 moles per mole).

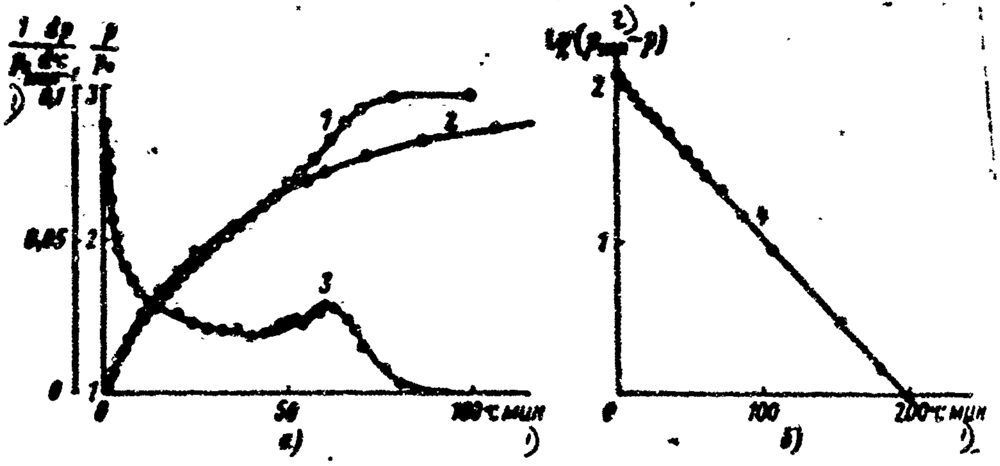

Fig. 8. Kinetics of disintegration of glycoldinitrite at 180°.
p_o; 1 - and 3 - 299; 2 and 4-65.6 mm Hg, a - in coordinates p/p_o - τ and v - τ; b - in coordinates log (p_{con} -p) - τ.
1) minutes; 2) log (p_{con} - P).

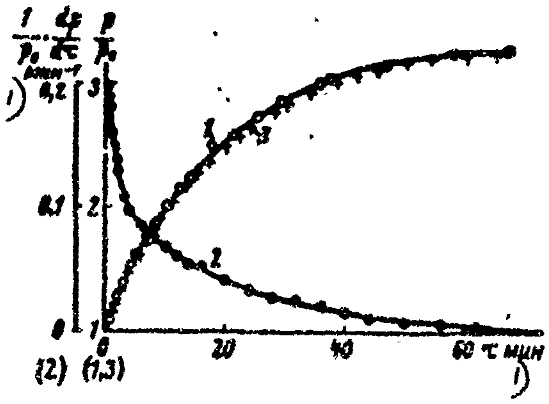

Fig. 9. Kinetics of disintegration of glycoldinitrite at 190°.
p_o: 1 and 2-143; 3-305 mm Hg 1) minutes.

Influence of Nitric Oxide[1]

Addition of nitric oxide (see Fig. 10, 11 and Table 1) considerably decreases initial speed of growth of pressure[2], and besides the effect of addition of each new NO is less than the preceding, and upon achievement of certain maximum concentration of nitric oxide disappears entirely. At an increase of temperature this maximum concentration somewhat is increased, and the effect of

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[1] In carrying out experiments with the addition of NO student B. I. Komkov took part.

[2] Initial speed of gas formation decreases also upon addition of NO_2 to dinitrite.

addition of NO decreases (Fig. 11).

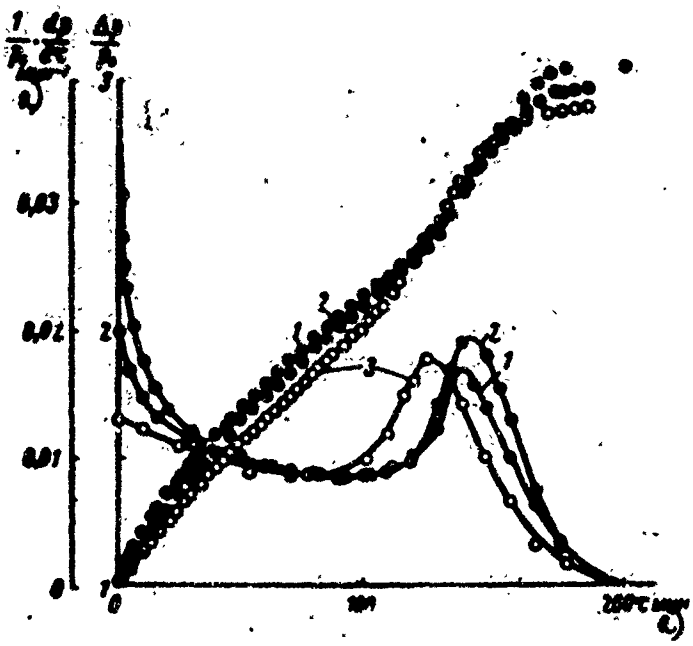


Fig. 10. Influence of nitric oxide on disintegration of glycoldinitrite at 170° and $p_0 = 250 - 260$ mm Hg
p_{NO}: 1 - 0; 2 - 25; 3 - 62 mm Hg ($\Delta p = p - p_{NO}$). a) minutes.

It is necessary to note that lowering of initial speed depends not on the relationship between concentrations of dinitrite and nitric oxide, but only on the concentration of NO (see Table 1).

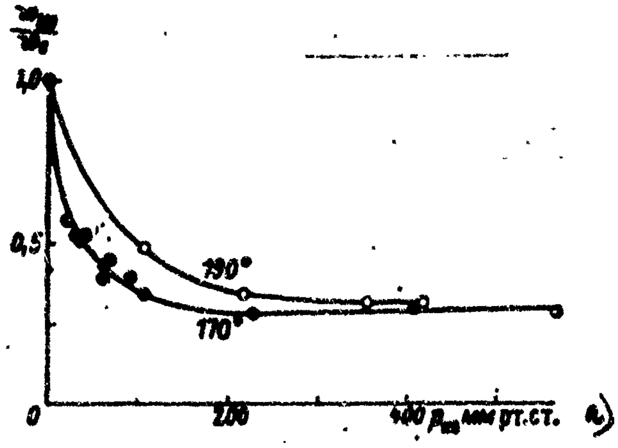


Fig. 11. Dependence of initial speed of gas formation at disintegration of glycoldinitrite at 170 and 190° on pressure of nitric oxide. On the axis of ordinates - the relation of initial speed of gas formation in the presence of NO to initial speed with that same temperature without addition of NO.
a) p_{NO} mm Hg.

It is essential also that, in significantly decreasing initial speed, nitric oxide, added in moderate (to ~200 mm) quantities, practically does not affect the speed of the following stages of disintegration (see Fig. 10).

Table 1

Influence of nitric oxide on initial speed of gas formation during thermal disintegration of glycol dinitrite at 170°

Начальное давление окиси азота $[NO]_0$ в мм рт. ст. 1)	0	22	25	34	37	41	62	63	67	92	107	228	409	586
Начальное давление динитрита P_0 в мм рт. ст. 2)	—	169	257	399	361	570	260	1024	295	232	573	281	710	313
$[NO]_0/P_0$ 3)	—	0,130	0,097	0,085	0,105	0,072	0,238	0,062	0,227	0,396	0,187	0,812	0,576	1,87
Начальная скорость роста давления (w_0 мин$^{-1}$)$\cdot 10^2$ 4)	3,5	2,00	2,09	1,84	1,81	1,83	1,41	1,82	1,87	1,38	1,23	1,01	1,07	1,03

1) Initial pressure of nitric oxide $[NO]_0$ in mm Hg; 2) Initial pressure of dinitrite P_0 in mm Hg; 3) $[NO]_0 / P_0$; 4) Initial speed of growth of pressure (w_0 min^{-1}) $\cdot 10^2$

Composition of Gaseous Products of Disintegration

The results of analysis of gaseous final products of disintegration of ethylene glycol dinitrite at 170° are given in Table 2. A very significant fact is the presence of significant quantities of carbon dioxide in gases. With a very large initial concentration of dinitrite vapors on the second stage of disintegration a temporary yellowing the gas phase is observed, indicating the formation of nitrogen peroxide. If the temperature on the second state is quickly lower from 170 to 100°, then formation of ever increasing quantities of NO_2 can be noted also at usual concentrations of glycoldinitrite. NO_2 is detected in intermediate products at decreased concentrations of dinitrite also if disintegration from the very beginning takes place at low (120°) temperature.

One should note that a change in initial pressure, addition of nitric oxide and water hardly influences the composition of final gaseous products of disintegration

Table 2

Composition of gaseous final products of disintegration of dinitrite of ethylene glycol at 170°

1) Начальное давление динитрита, *мм* рт. ст.	Вещество, добавленное к динитриту 2)	Начальное давление добавленного вещества *мм* рт. ст. 3)	$P_{кон}/P_0$ при температурах 4)			Молей газа на на моль динитрита 5)				
			170°	100°	комнатной 6)	NO	N_2O	CO	CO_2	N_2
184	—	—	3,00	2,54	2,08	1,54	0,10	0,16	0,22	0,06
276	—	—	2,89	2,44	2,10	1,55	0,13	0,15	0,19	0,08
390	NO	34	2,92	2,46	2,18	1,46	0,16	0,25	0,25	0,06
250		62	2,92	2,43	2,16	1,52	0,12	0,18	0,27	0,07
295		67	2,91	2,44	2,16	1,46	0,17	0,20	0,28	0,05
281		228	2,88	2,40	2,15	1,50	0,16	0,22	0,21	0,06
291	H_2O	67	—	—	—	1,57	0,12	0,25	0,21	0,03

1) Initial pressure of dinitrite, mm Hg; 2) Substance added to dinitrite; 3) Initial pressure of added substance, mm Hg; 4) P_{con}/P_o at temperatures; 5) Moles of gas per mole of dinitrite; 6) Room.

Condensing Products of Disintegration

Condensing at room temperature after termination of experiments with quite high (more than ~200 mm at 170°) initial pressure, the colorless viscous liquid, turning brown with continued heating, dissolves well in water and has an acid reaction on litmus paper. It contains glycol acid (test with solution of $FeCl_3$ and phenol in water [8] and test with 2.7 - dioxynaphthalene) and, apparently, glycol aldehyde (yellowing of aqueous solution of products upon addition of several drops of concentrates alkali [23]). Oxalic acid (test with $CaSO_4$ and test with diphenylamin [26]) and ethylene glycol (reaction borax and test with $CuSO_4$ in alkaline medium [4]) in it are not detected.

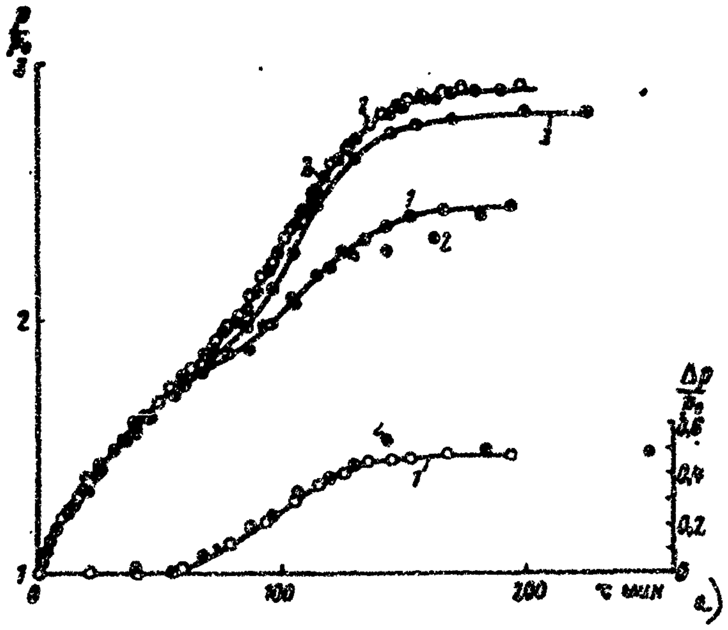


Fig. 12. Kinetics of formation at disintegration of glycoldinitrite of products, not condensed at 170° and condensed at 100°. Temperature of experiment 170°.
Products, not condensed at 170 and 100° - upper and middle curves, condensed at 100° - lower curve (axis of ordinates on the right).
P_0: 1 - 332, 2 - 302, 3 - 332 mm Hg (experiment vessel at 170° and pressure at 100°. All pressures are expressed in mm Hg at 170°.
a) minutes.

In the products there is also water and formaldehyde, and the quantity of the latter, apparently, is greater, the higher the temperature of the experiment.

Experiments were also conducted in determining the kinetics of formation at disintegration of dinitrite of ethylene glycol of products, condensed at lowering of temperature. In these experiments the reaction vessel, heated at 170°, from time to time was quickly cooled to 100°, pressure was measured with this temperature and again was quickly heated to the temperature of the experiment. Curves, obtained in these experiments are shown in Fig. 12 - 13. It is clearly evident that difficulty-volatile products will be formed exclusively on the second stage of decomposition, and an increase of pressure affects their formation only in that measure, in which it affects the course of the second stage (approximating the moment of its approach and increasing the speed of the reaction).

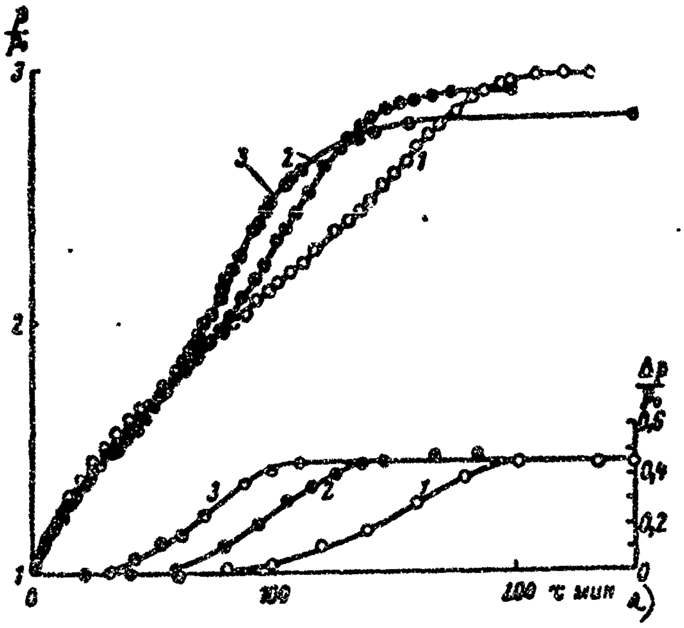


Fig. 13. Kinetics of formation of products of disintegration of glycoldinitrite, condensed at 100°, in experiments at 170°. P_0: 1 - 184, 2 - 322, 3 - 535 mm Hg, p - concentration of products, condensed at 100°, expressed in mm Hg at 170°.
a) minutes.

Addition to Glycoldinitrite of Condensed Products of Disintegration and Increase of Surface

Addition of products of disintegration condensing at room temperature to glycoldinitrite and increasing the relationship of the surface of the reaction vessel to its volume originally affects gas formation. Addition of one of the condensed products - water (Fig. 14) and increase of surface by filling the vessel with glass tubes (Fig. 15) do not render an influence on the speed of initial stages of disintegration, however on the middle stages curves in these experiments are noticeably higher than usually, which indicates an increase of "specific gravity" of reactions of the second stage. Addition of final products of disintegration condensing at room temperature, which are very hygroscopic and, in spite of prolonged evacuation, apparently, contain little water, even more strongly influences the second stage and somewhat accelerates the first (Fig. 16). The most effective of all on disintegration influences the joint presence of significant quantities of water and condensing products: initial speed increases several times and the reaction usually is twice as fast as in experiments with pure dinitrite (Fig. 17).

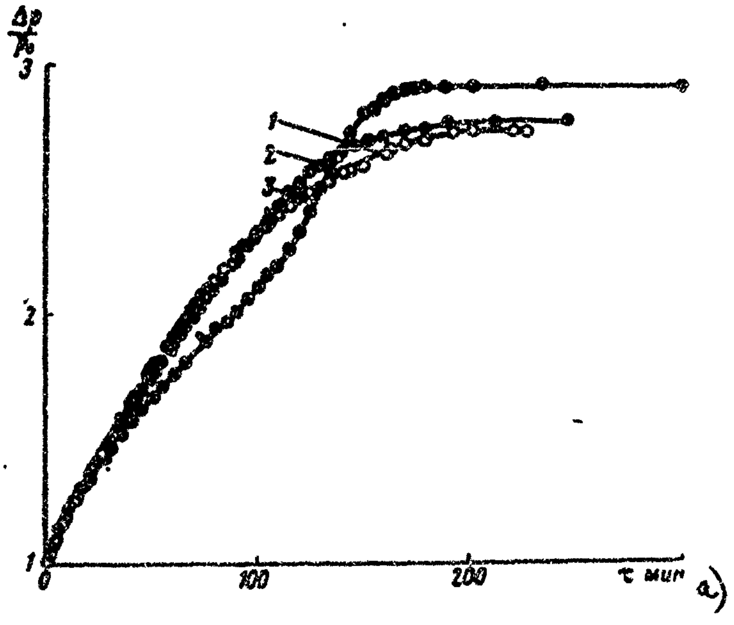


Fig. 14. Influence of water on disintegration of glycodinitrite at 170° and $p_0 \approx$ 260 - 290 mm Hg.
p_{H_2O}: 1 - 78, 2 - 67, 3 - 0 mm Hg, ($\Delta p = p - p_{H_2O}$). a) minutes

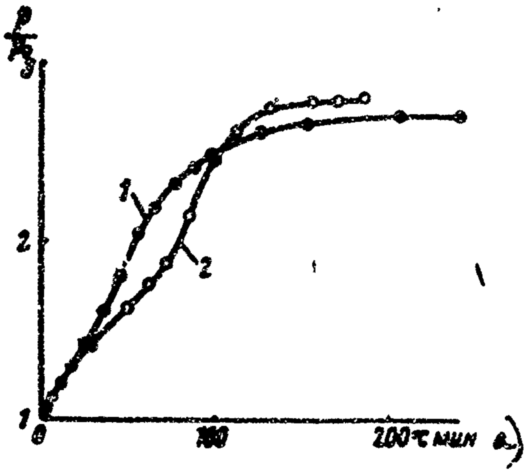


Fig. 15. Influence of magnitude of surface on decomposition of glycoldinitrite at 170° and $p_0 \approx 500$ mm Hg. s/v: 1 - 10, 2 - 2 cm^{-1}. a) minutes.

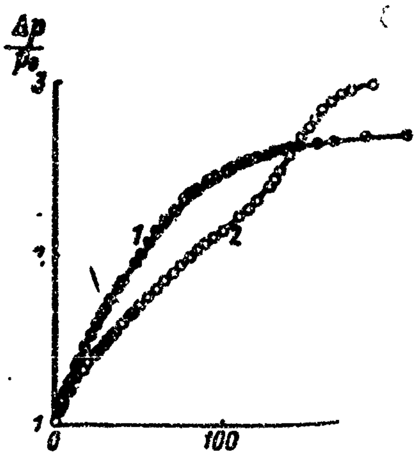


Fig. 16. Influence of final products of disintegration condensed at room temperature on decomposition of glycoldinitrite at 170°. 1 - p_0 = 220 mm Hg, with addition of products of disintegration, 2 - p_0 = 248 mm Hg, pure glycoldinitrite.

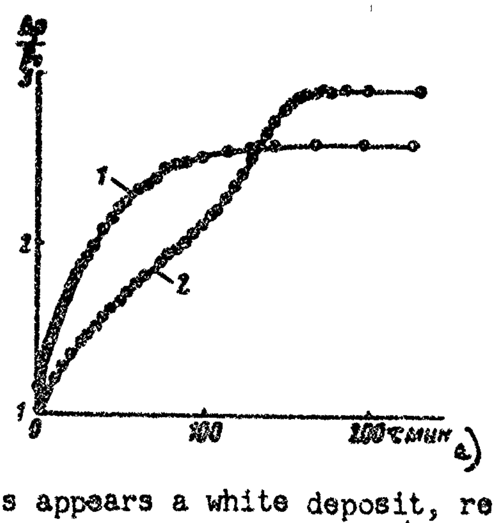


Fig. 17. Influence of final products of disintegration condensed at room temperature and water on decomposition of glycoldinitrite at 170°. 1 - with addition of products of disintegation and water (p_0 = 280; p_{H_2O} = 100 mm Hg); 2 - pure glycoldinitrite (p_0 = 276 mm Hg). a) minutes.

On the walls of the vessel in these experiments appears a white deposit, replaced upon cooling by a thin layer of colorless transparent liquid. The gas phase in the beginning of the experiments turns yellow or brown and is then slowly bleached.

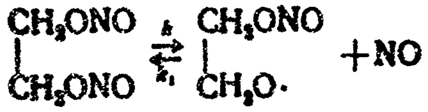
Mechanism of Thermal Decomposition Ethylene Glycol Dinitrite

Diphase Character of Disintegration

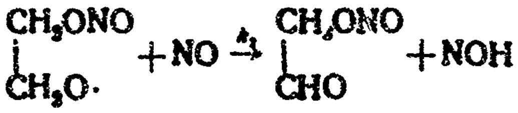
The data obtained during the study of thermal decomposition of dinitrite of ethylene glycol show that disintegration even of this simplest polynitrite is very complicated.

As was already noted above, the character of kinetic disintegration curves at not very high temperature and sufficiently great initial concentration indicates that decomposition includes at least two macroscopic stages [16] divided in time, each of which, obviously, consists of several elementary reactions. This assumption is confirmed by a number of other experimental data: significant influence of initial concentration, and also filling of the reaction vessel with glass tubes on the second stage of disintegration and very weak - on the first; essential influence of nitric oxide on the first stage and practical absence of such an influence on the second; appearance on the second stage of difficultly-volatile products of disintegration and nitrogen peroxide and their absence on the first etc.

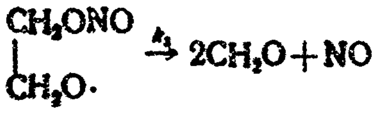
First stage of disintegration. The proximity of activation energy of the reaction, determining the initial disintegration rate of glycoldinitrite (36 kilocalories mole) to magnitudes, received for mononitrites (34 - 38 kilocalories mole - see Table 3 on page 459), the formation of NO and N_2O, the similarity of the character of influence of NO on the initial disintegration rate of glycoldinitrite with those mentioned by Levy for isopropylnitrite [38] and several other facts permit the assumption that the mechanism of initial stage of decomposition of dinitrite is similar to the mechanism of disintegration of mononitrites, adopted by Levy [37], [38] and includes the following main reactions:



$$\begin{array}{l}CH_2ONO\\ |\\ CH_2ONO\end{array} \underset{k_1}{\overset{k}{\rightleftarrows}} \begin{array}{l}CH_2ONO\\ |\\ CH_2O\cdot\end{array} + NO \qquad (11)$$



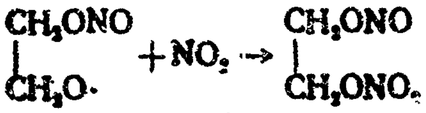
$$\begin{array}{l}CH_2ONO\\ |\\ CH_2O\cdot\end{array} + NO \xrightarrow{k_2} \begin{array}{l}CH_2ONO\\ |\\ CHO\end{array} + NOH \qquad (12)$$



$$\begin{array}{l}CH_2ONO\\ |\\ CH_2O\cdot\end{array} \xrightarrow{k_3} 2CH_2O + NO \qquad (13)$$

$$2NOH \rightarrow N_2O + H_2O \qquad (14)$$

In presence of NO_2 this reaction is possible also



$$\begin{array}{l}CH_2ONO\\ |\\ CH_2O\cdot\end{array} + NO_2 \rightarrow \begin{array}{l}CH_2ONO\\ |\\ CH_2ONO_2\end{array} \qquad (15)$$

Kinetic processing of equations (11) - (13) on the assumption that concentration of radical $CH_2 \cdot ONO \cdot CH_2O \cdot$ is stationary, gives the followi expression for speed of change of pressure on the first stage

$$\frac{dp}{d\tau} = \frac{k_2[NO] + 3k_3}{(k_1 + k_2)[NO] + k_3} \left[\begin{array}{l}CH_2ONO\\ |\\ CH_2ONO\end{array}\right].$$

for initial speed of gas formation during disintegration we have

$$w_0 = \frac{1}{p_0}\left(\frac{dp}{d\tau}\right)_0 = 3k, \quad \text{or} \qquad k = \frac{1}{3} w_0.$$

This is coordinated with its independence on concentration and allows to determine the constants of speed by the initial speeds of gas formation, anc constants B and E of Arrhenius equation for k. Using the data, shown on pa 305, we obtain

$$k = 10^{13.8} \exp(-35.6 \cdot 10^3/RT) \text{ sec}^{-1}.$$

The magnitude of 35.6 kilocalories mole, apparently, equals the energy of breaking the bond O - NO in dinitrite of ethylene glycol. The exponent in this case is the same as alkylmononitrites (see Table 3), and in distinction from many nitrates [1] has a normal value.

For experiments with addition of nitric oxide initial speed of gas formation is determined by the expression

$$w_0^{NO}=\frac{1}{p_0}\left(\frac{dp}{d\tau}\right)_0=k\,\frac{k_2[NO]_0+3k_3}{(k_1+k_2)[NO]_0+k_3}. \qquad (16)$$

Hence, in particular, it follows that in accordance with the experiment the initial speed depends not on the relationship between concentrations of NO and dinitrite, but only on the concentration of NO and that with an increase of this concentration it decreases, approaching to a limited value, equal to $\frac{kk_2}{k_1+k_2}$.

owing

Subtracting from equation (16) the relationship $w_0 = 3k$, after conversions we obtain

$$\frac{[NO]_0}{w_0-w_0^{NO}}=\frac{k_3}{k(3k_1+2k_2)}+\frac{k_1+k_2}{k(3k_1+2k_2)}[NO]_0 \qquad (17)$$

Considering expression (17), we see that in case of applicability of the postulated mechanism to the first stage of disintegration of glycoldinitrite we should for experiments with addition of a different quantity of nitric oxide obtain a straight line $x = A+B[NO]_0$ in coordinates:

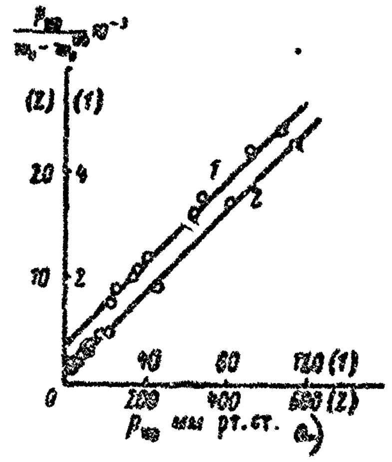


Fig. 18. Influence of nitric oxide on initial speed of gas formation at disintegration of glycoldinitrite at 170°.
1 - internal scale, 2 - external scale. a) mm Hg.

and also

page

In Fig. 18 the dependence between concentrations of NO and initial speed is represented in coordinates $[NO]_0$, x. As can be seen, in the whole range of concentrations of NO the points are well packed on the straight line. Coef of the equation of this straight line, calculated by the method of smallest quadrants, are equal: $A = 6.6 \cdot 10^{2}$ mm · min, B = 39.3 minutes. Knowing the and also considering that $k = 1.9 \cdot 10^{-4}$ sec^{-1}, and limiting value $\varpi_{0}^{NO} = \frac{k_1}{k_1 +}$ $1.7 \cdot 10^{-4}$ sec^{-1}, it is possible to calculate the ratio of constants of spe of secondary reactions of the first stage. We obtain: $k_2/k_1 \approx 6$, $k_3/k_1 \approx 1$ i.e. $k_3 > k_2 > k_1$ (concentration in mm Hg).

We recall that at disintegration of ethylnitrite close to 200° [37] observed a reverse relationship between the speeds of corresponding reacti (see footnote on page 424).

This mechanism explains also the formation of formaldehyde, nitric an nitrous oxide at disintegration of glycoldinitrite, the influence of NO_2 o initial speed and several other facts. If one were to consider detachment nitric oxide oppressing its action and the existence of maximum concentrat NO, then it is easy to explain the observed self-braking of the reaction o first stage and dependence of its degree on initial concentration of dinit

Second stage of disintegration. However, the main peculiarity of the disintegration of glycoldinitrite -- its clearly expressed diphase charac upon increasing concentration -- that mechanism offered for interpretation one of the classic monomolecular reactions, naturally, cannot be explained The way to explanation of the peculiarities of the second stage of disinte is indicated by experiments in determining the kinetics of formation of di volatile products and the addition of these products to fresh dinitrite.

if one were to compare the accelerating action of difficulty-volatile proc

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[1] By analogy with disintegration of alkylmononitrites it may be concl that the sequence of reactions (11)- (14) by far does not exhaust an enti variety of transformations, occurring on the first stage of disintegratio glycoldinitrite and including, possibly, disintegration of mononitrites, interaction of hydroxyradical with carbonyl compounds, nitroxyl etc. How experimental data, requiring postulating of these steps, is too small mea

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with the fact that they will be formed at the stage of self-acceleration of disintegration faster, as the speed of gas formation on this stage is higher, then it will be natural to assume that self-acceleration of decompositions of glycoldinitrite is explained by the catalytical action of these products.

Comparing these observations with the formation of nitrogen peroxide in intermediate, and carbon dioxide and organic acids - in the final products of disintegration, and also with influence on disintegration of water (itself and in combination with other products)and the easy hydrolyzability of dinitrite in liquid state, we assumed that the reaction of catalyzed difficulty-volatile products, is the interaction of glycoldinitrite and can be the intermediate products of its disintegration with water, initially formed, for example, by reaction (14).

This interaction, similar to low-temperature hydrolisis of nitrites, leads to replacement of the nitrite group by a hydroxy group[1] and formation of nitrous acid. The latter is decomposed into nitric oxide and nitrogen peroxide and water. Nitrogen peroxide oxidizes the large excess of organic products and yields CO, CO_2 and a certain additional quantity of water, and also other substances, including organic acids.

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[1] The absence in products of disintegration of significant quanitites of ethylene glycol can be explained by the fact that at high temperature it is very quickly oxidized by nitrogen peroxide. Experiments on oxidation of glycol by NO_2 at 150° confirmed this assumption and showed, in addition, that in the gaseous products of oxidation the concentration of CO_2 is significantly greater, than CO (cf. Table 2). We recall that at oxidation by nitrogen peroxide of formaldehyde and glyoxal (main organic products of disintegration of dinitrite in the case when it wholly followed the mechanism of Levy) a reverse relationship between concentrations of CO and CO_2 is observed

It is difficult to assume, so that the reaction of hydrolytic character is accomplished in volume. Reactions of interaction of nitrites with water are ionic processes, the speed of passage of which in gas phase in usual conditions is insignificantly small.

The influence of surface on self-acceleration and catalysis of decomposition namely with difficulty-volatile products indicate that these reactions take place on the wall of the vessel in a fine film of liquid covering.

Difficultly-volatile products, settling on the surface of the glass and absorbing molecules of dinitrite and water, facilitate and accelerate their interaction. Probably, the acid character of certain products also plays a part[1].

It is interesting to note that the appearance in products of disintegration of nitric oxide, substantially decreasing the speed of gas formation, very little affects the disintegration rate of nitrite (at 170° $k = 1.9 \cdot 10^{-4}$ sec^{-1}, and the limiting value of the constant of speed in the presence of NO: $\frac{k\,k_2}{k_1+k_2} = 1.7 \cdot 10^{-4}$ sec^{-1}). In connection with this, the influence of initial concentration of dinitrite on the speed of the first stage of disintegration is very small. On the base of the second stage are the polymolecular reactions, therefore at an increase of concentration of dinitrite the speed and role of reactions of this stage in the process of decomposition considerably increase.

Thermal Decomposition of Trinitrite of Glycerine

(A work, the result of which are given in this division, were carried out jointly with Ye. V. Vasil'ev)

Obtainment and Certain Properties of Glycerine Trinitrite

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[1] The interaction of dinitrite with products of disintegration, besides direct experiments of addition of products is indicated also by the fact that at sufficiently great concentration of dinitrite the time of decomposition is significantly (2 - 3 times)less than that, which is required for completion of a monomolecular reaction of disintegration.

Trinitrite of glycerine was obtained by O. Masson's method [39], by passing through dynamite glycerine, poured into a water cooled glass cylinder, a strong current of a mixture of nitric oxide and nitrogen peroxide. A mixture of oxides in turn was obtained, adding air to gas, emanating under the action of sulphuric acid on sodium nitrite. The product was dried by sodium sulfate and three times was sublimated in a current of nitrogen at 60 - 100°, removing every time on the average 0.6 - 0.8 distillate. Then the nitrite was evacuated for removal of gases dissolved in it and in a vacuum was transferred into ampoules, which were then kept in a dark cold place. Pure nitrite is a light-yellow mobile liquid with a characteristic odor. Upon storage in air for the duration of 2 - 3 days it is decomposed, is colored dark-green, and is kept in sealed ampoules for the duration of 2 - 3 months.

Results of elementary analysis of a freshly-distilled product:

Found %: C - 20.20; 20.29; H - 2.90; 3.00[1]. Calculated % for $C_3H_5O_6N_3$: C - 20.11; H - 2.79.

Determination of molecular weight, done by manometric method, gave in two experiments the value 181.5 and 178 (calculated molecular weight - 179).

The dependence of vapor tension on temperature in the range 0 - 130° is represented in Fig. 19. Heat of evaporation, determined by the slope of the straight line in coordinates $\lg p - \frac{1}{T}$, constitutes 10.1 kilocalories mole, the boiling point, obtained by extrapolation of the curve of pressure - temperature on 760 mm Hg is equal to 154° according to Masson [39] approximately 150°). Temperature of hardening from - 60 to - 58°C.

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[1] Reliable determinations of nitrogen in trinitrite were not able to be conducted.

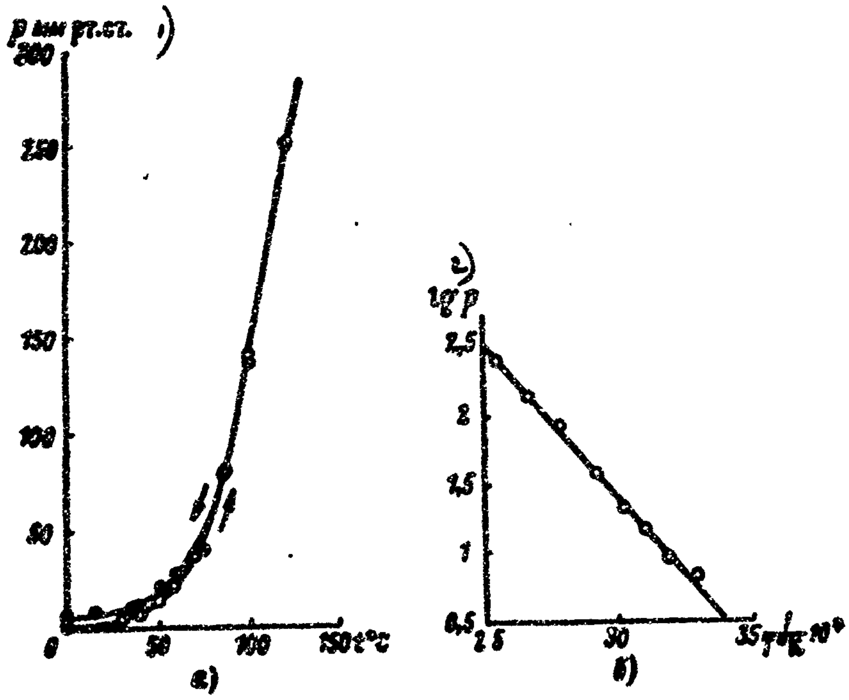

Fig. 19. Dependence of vapor tension of glycerine trinitrite on temperature.
a - in coordinates p-t; b - in coordinates lg p - $\frac{1}{T}$.

1) p mm Hg; 2) log p.

The methodology of preparation and carrying out of experiments on thermal decomposition of glycerine trinitrite basically is analogous to what is above described for glycolditrite.

Results of Experiments

Influence of Initial Concentration

Experiments on thermal decomposition of glycerine trinitrite were conducted at 100 - 160°. The influence of initial concentration on disintegration was especially in detail investigated at 150°. Kinetic curves, obtained with this temperature, are shown in Fig. 20.

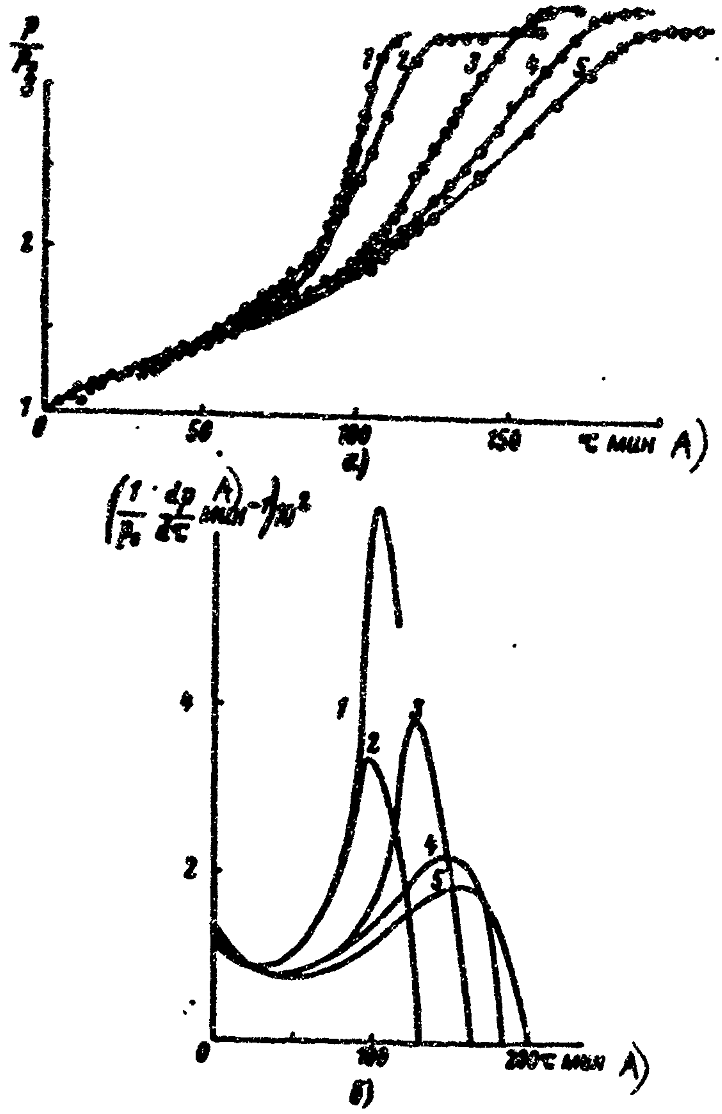

Fig. 20. The kinetics of gas formation in disintegration of glycerine trinitrite at 150°.
p_0 : 1 - 545; 2 - 310; 3 - 215; 4 - 142; 5 - 69 mm Hg.
a - in coordinates $p/p_0 - \tau$; b - in coordinates $w - \tau$.
A) minutes.

Their similarity with the curves, obtained for dinitrite of ethylene glycol, for example, at 170° is completely obvious: the clear diphase character of decomposition with fall of speed on the first stage and growth - on the second, independence of initial speed from concentration, increase at increase of concentration of maximum speed and decrease of the time of its achievement allow us to talk about this with sufficient definiteness. Certain distinctions are also clearly evident. At near times of full decomposition the role of reactions of the second stage at disintegration of trinitrite is significantly larger than at disintegration of dinitrite: the relation of maximum speed to initial at $p_0 \sim 200$ mm, for example, in the first case is approximately 3 (150°), in the second - nearly 0.4 (170°). Speed on the first stage of decomposition falls less sharply, than in the case of glycoldinitrite, and the oppressing influence of initial concentration on speed of the first stages of disintegration is not developed.

The gas phase on the second stage of decomposition in usual concentrations of trinitrite is colored light-yellow(in the case of dinitrite with these concentrations it is not colored even at 140°). The quantity of final products, not condensed at the temperature of the experiment, is somewhat (nearly one mole per mole of parent substance) larger, than in disintegration of dinitrite. The quantity of final products, condensed upon lowering of temperature to room, constitutes $\sim$0.4 moles per mole.

Influence of Temperature

A change of temperature affects disintegration of glycerine trinitrite the same as disintegration of dinitrite of ethylene glycol: upon lowering the temperature the role of reactions of the second stage is increased, the relationship between speed on maximum and initial increases (at $p_0 \sim 300$ mm $(w_{max}/w_o)_{143°} = 5.4$; $(w_{max}/w_o)_{160°} = 2.2$). Upon lowering the temperature the content of nitrogen peroxide is also increased in products of the second stage of disintegration. Only slightly yellow at 150 - 160°, the gas phase at 100° near to the maximum of speed becomes brick-red.

Upon significant (to 100 - 120°) lowering of temperature, the character of decomposition somewhat changes: speed on the initial stage does not decrease, but slowly increases, and the curve is transformed into a kinetic curve of usual autocatalytic reaction (Fig. 21).

In considering the similarity between disintegrations of dinitrite of ethylene glycol and trinitrite of glycerine, we conducted an experiment on decomposition of dinitrite at low temperature in hope of also obtaining for it the usual autocatalytic curve with one extreme value of speed. These expectations were justified: at 120° (Fig. 22) dinitrite was decomposed with a constantly increasing speed, on the maximum exceeding the initial speed by 17 times. The gas phase near to maximum was colored bright-yellow.

Initial speed of gas formation at 143 - 160° grows with a temperature somewhat faster, than in the case of glycoldinitrite (at 170 - 190°), activation energy upon calculation according to initial speeds in this range of temperatures constitutes 41.4 kilocalories mole[1] (Fig. 23). The exponent is also high: $10^{17.8}$ sec^{-1}.

At 120° initial speed is considerably higher than this is required by Arrhenius equation; apparently, with this temperature the second stage starts to be placed on the first.

(See Fig. 21 On Following Page)

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[1] It is necessary to note that in this respect the investigated polynitrites are completely analogous to corresponding polynitrates: dinitrite and dinitrate [2] of glycol have activation energy of disintegration of approximately 36 kilocalories mole, trinitrite and trinitrate [2] of glycerine - 41 - 43 kilocalories mole. The cause of this distinction between di- and trinitrates and nitrites are still insufficiently clear.

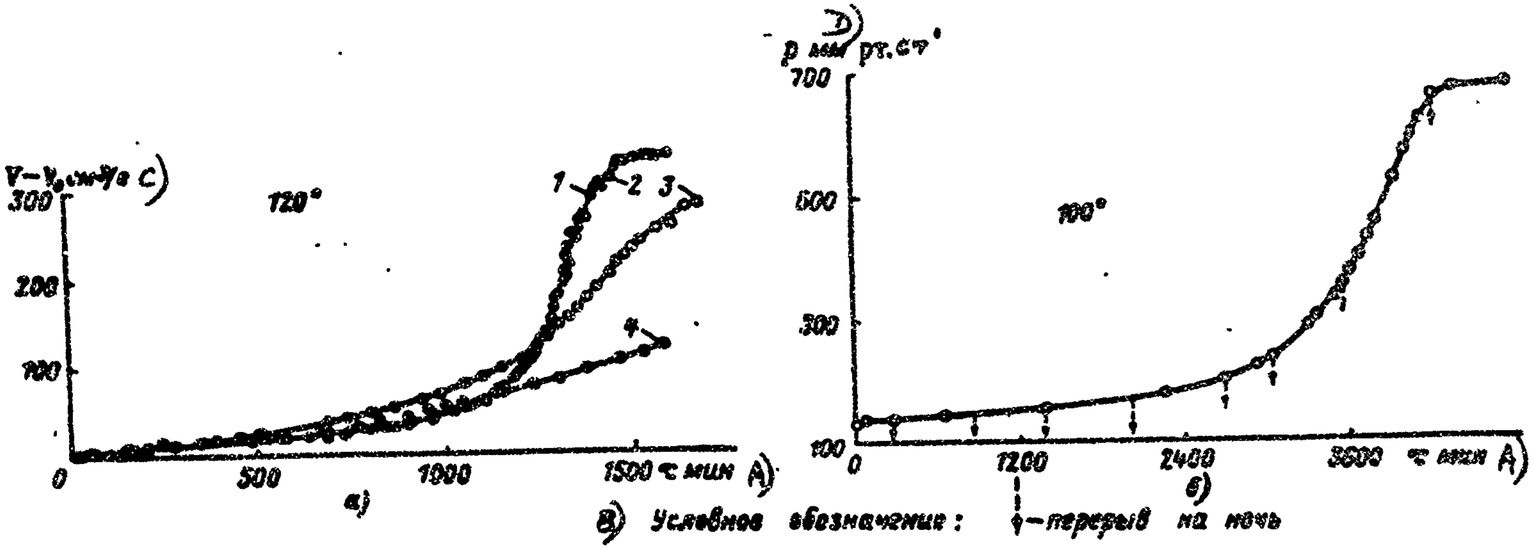

Fig. 21. Disintegration of Glycerine Trinitrite at 120 and 100°.

a − (m/v g/cm^3) · 10^4 : 1 − 26.9; 2 − 30.6; 3 − 10.8 (p_o = 148 mm Hg); 4 − 5.2 (p_o = 72 mm Hg). In experiments 1 and 2 a certain part of the substance in beginning of the experiment is in liquid phase; (V − V_o) − difference between volume of gaseous products in the vessel in a given moment of time, and initial volume of trinitrite vapors; b − m/v = 15 · 10^{-4} g/cm^3, in the beginning of the experiment approximately one third of the substance is in liquid phase.
A) min; B) Conditional designation: ↓ − break for the night; C) V − V_o cm^3/g; D) p mm Hg.

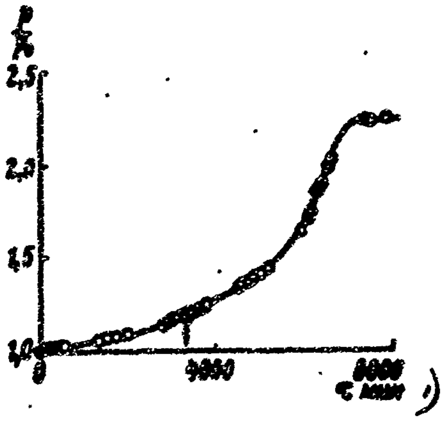

Fig. 22. Disintegration of dinitrite of ethylene glycol at 120° and p_o = 780 mm Hg. 1) minutes.

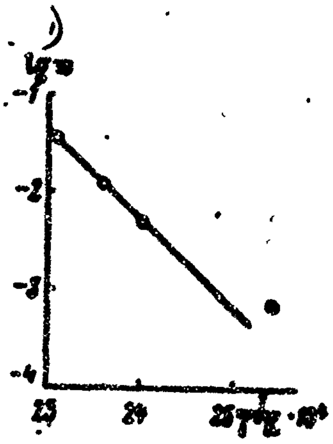

Fig. 23. Dependence of initial speed of gas formation in disintegration of glycerine trinitrite on temperature in the range 120 - 160°.
1) log w.

Influence of Nitric Oxide

Addition of nitric oxide to trinitrite of glycerine just as to dinitrite of glycol, decreases the speed of gas formation on the first stage and almost does not affect the second. The character of decrease of initial speed upon addition of increasing quantitites of NO (Fig. 24) is similar to that, which is observed for dinitrite.

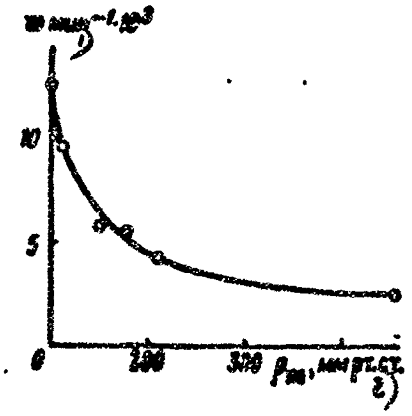

Fig. 24. Influence of NO on initial speed of gas formation during disintegration of glycerine trinitrite at 150°. 1) minutes. 2. mm Hg.

Addition to trinitrite of large quantities of NO decreases the initial disintegration rate in a limit approximately 4 times versus 3 in the case of glycoldinitrite at 170 - 190°. It is true that this limited suppression of gas formation is attained upon addition of not less than 500 mm of NO, just as for decreasing the speed to the limit in the case of dinitrite at 170°, 20 mm of this gas is sufficient (see Fig. 11).

Final Products of Disintegration and their Influence on the Process of Decomposition

Condensed at room temperature, the final products of disintegration[1] - a dark brown liquid, somewhat less viscous, than in the case of dinitrite, are well dissolved in water and have an acid reaction on congo red. Titrating an aqueous solution of these products with an alkali showed that on carboxyl groups is replaced nearly 0.1 of all - ONO groups, contained in trinitrite.

Addition of final condensed products to fresh nitrite,as Fig. 25 shows, considerably increases speed and changes the character of disintegration, turning the self-accelerated reaction into a quickly delayed one.

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[1] Gaseous products of disintegration were not analyzed. We only know that nitric oxide constitutes a significant share of them, yielding a strong brown color in the gas phase upon taking in air into the vessel.

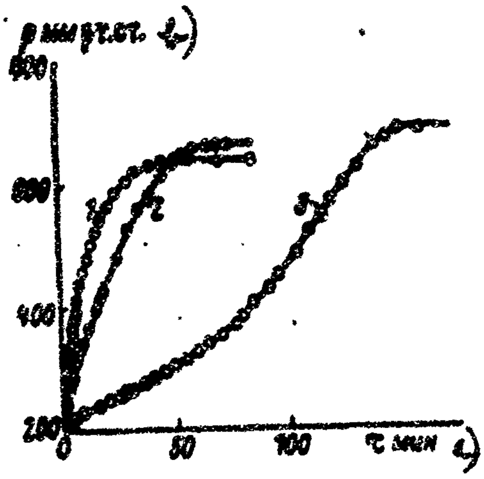

Fig. 25. Influence of condensed products of disintegration on decomposition of glycerine trinitrite at 150°.
1 - and 2 - trinitrite with addition of condensed products, 3 - fresh nitrite. a) minutes; b) p mm Hg.

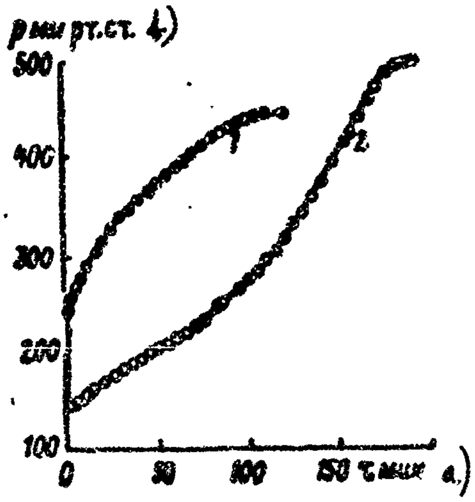

Fig. 26. Influence of water on disintegration of trinitrite of glycerine at 150°.
1 - p H_2O = 45 mm Hg, 2 - without addition of water. a) minutes; b) p mm Hg.

These experiments were conducted in the following way. Condensed products from the preceding experiment dissolved in a small quantity of water, were placed in a pure reaction vessel and evacuated for a long time, heating it to 80 - 100° for removal of water. After that trinitrite was introduced into a special outlet sealed to the vessel, then the latter was unsealed and placed in a thermostat.

It is necessary to note that in spite of prolonged preliminary evacuation, the condensed very hydrophilic products, apparently, still retain a little water. In one of two experiments (curve 2), shown in Fig. 25, water was removed more thoroughly, than in the other. The speed of decomposition in this experiment correspondingly was lower.

It is necessary to say that in spite of specially taken measures of preventing the interaction of added substances with liquid (not managing yet to be turned into vapor) nitrite in the process of heating the reaction vessel to the temperature of the thermostat, the reaction in liquid phase all the same, apparently, proceeded and could influence the course of the experiment.

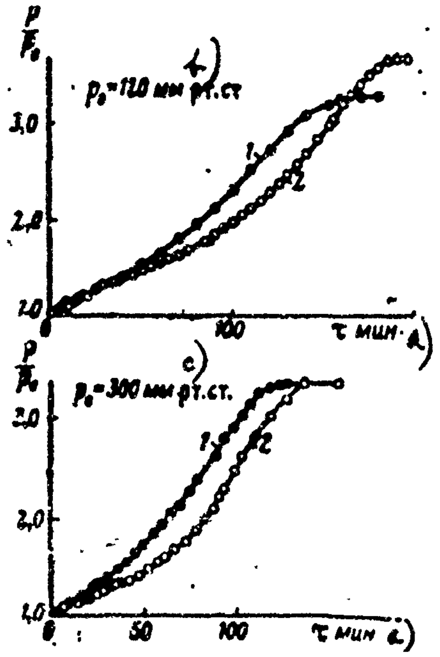

Fig. 27. Influence of the relation of the surface of the vessel to its volume on disintegration of glycerine trinitrite at 150°.
s/v: 1 - 10; 2 - 2 cm^{-1}. a) minutes; b) p_0 = 120 mm Hg, c) mm Hg.

Increase of the relation of the surface of the reaction vessel to its volume (Fig. 27) just as during disintegration of dinitrite noticeably approached the second stage and almost did not affect initial speed of gas formation.

Discussion of Results

It is hardly possible to doubt, comparing results of experiments, conducted with glycerine trinitrite and glycoldinitrite, in deep similarity of mechanisms of their disintegration. First, what can one say with sufficient definitiveness - this is the diphase character of disintegration of these compounds.

Reactions of the first stage of decomposition of trinitrite, apparently, are analogous to reactions of disintegration of alkylmononitrites and glycoldinitrite on this stage, and the main ones include splitting of middle or extremely groups of NO, disintegration of hydroxyradicals and reactions of them with nitric oxide, disintegration of nitrites of hydroxyaldehydes and others formed with this.

Based on the results obtained recently [32] in the study of disintegration of 1, 3 - butylene glycol dinitrite, the middle NO - group of which splits 14 times faster than the extreme and also in the old experiments of Farmer [25] and Delpy [20], which discovered that upon saponification of nitroglycerine a basically symmetrical glycerine dinitrate is formed, one can expect that the speed of splitting of the middle NO - group in glycerine trinitrite is greater than the extreme groups[1]; there are not direct indications of this, however.

Experiments with additon of NO at 150° show that the disintegration rate of hydroxyradicals in the case of glycerine trinitrite,apparently, is higher than for glycoldinitrite (even at 190°). For maximum oppression of gas formation during decomposition of trinitrite it is necessary to add significantly more NO. This is confirmed by a less sharp fall of speed on the first stage of disintegration of trinitrite and the absence of oppression of gas formation upon increase of initial pressure. "Specific gravity" of reactions of radicals with NO, yielding nitroxyl, is correspondingly less than in the case of disintegration of dinitrite, apparently, even less than the role of reverse stage

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[1] This assumption contradicts the experiments with glycerine dinitrate conducted by Jelinek [7]. In these experiments it was shown that at 140-160° the speeds of disintegration of vapors of symmetric and nonsymmetric dinitrates differ little.

of the reaction of disintegration of a molecule of nitrite. Experimental data for a more detailed discussion of the mechanism of the first stage does not exist.

The second stage of decomposition of trinitrite, apparently, just as the second stage of disintegration of dinitrite, includes hydrolisis of the nitrite on the wall in a thin layer of condensed products covering it and oxidation of organic substances by nitrogen peroxide, formed during disintegration of nitrous acid.

The role of reactions of hydrolisis and oxidation during disintegration of glycerine trinitrite obviously is significantly greater, than in the case of decomposition of glycoldinitrite. This is indicated more greatly, than for glycoldinitrite, the growth of speed in the process of decomposition, formation of significant quantities of nitrogen peroxide under those conditions, with which there is not the slightest trace of it noticeably in the case of glycoldinitrite, significantly greater influence of water and condensed products of disintegration and so forth.

On the Mechanism of Thermal Decomposition of Esters of Nitrous and Nitric Acids

Esters of Nitrous Acid

Gasphase thermal disintegration of alkylmononitrites near 200° - one of the simple and studied in detail pyrolithic reactions. The most probable main stages of it - breaking the bond O - NO, interaction of the formed nitric oxide with a hydroxy radical and disintegration of the latter:

$$RCH_2ONO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RCH_2O\cdot + NO \xrightarrow{k_2} RCHO + NOH$$

$$RCH_2O\cdot \xrightarrow{k_3} R\cdot + CH_2O$$

Total speed of the process is determined by the speed of its first stage and changes according to the law of monomolecular reaction. Activation energy of this reaction is within the range 34 - 38 kilocalories mole, the pre-exponential factor in Arrhenius equation has normal value (10^{13} ./. 10^{14} sec^{-1}).

Increase and complication of a molecule in a series of alkylmononitrites leads to an increase of the disintegration rate. In Table 3 are the constants of Arrhenius equation and constants of disintegration rate of a series of mononitrites at 190°. It is clear that upon transition from one homologue to the next the speed of the reaction is increased approximately twice.

Table 3

Speed of thermal disintegration of alkyl nitrites

1) Вещество	2) Интервал температур °C	3) Энергия активации $E, \frac{ккал}{моль}$	4) lg B, (сек.$^{-1}$)	5) Начальная скорость распада и k при 190° сек.$^{-1}\cdot 10^4$	6) Ссылки на литературу
7) Метилнитрит	190—241	36,4	13,26	0,97; 0,48	[46]
8) Этилнитрит	190—241	37,7	14,14	1,89; 0,94	[47]
»	161—201	37,5	13,79	—	[37]
»	430—530	34,3±3	—	—	[44]
9) н-Пропилнитрит	170—210	37,65	14,44	3,95; 1,98	[48]
»	200—230	34,7	13,20	—	[13]
10) Изопропилнитрит	170—210	37,0	14,10	3,70; 1,85	[49]
11) н-Бутилнитрит	170—212	37	14,48	8,88; 4,41	[56]
»	202—239	36,2	13,65	—	[13]
12) Динитрит этиленгликоля	170—190	35,6	13,8	33; 11	
13) Тринитрит глицерина	143—160	41,6	17,8	140*; 47	

* По расчету.

1) Substance; 2) Range of temperatures °C; 3) Activation energy E, $\frac{\text{kcal}}{\text{mole}}$; 4) log B, (sec.$^{-1}$); 5) Initial disintegration rate and k at 190° sec.$^{-1}$ · 10^4; 6) References in literature; 7) Methylnitrite; 8) Ethylnitrite; 9) n - Propyl nitrite; 10) Isopropyl nitrite; 11) n - Butylnitrite; 12) Dinitrite of ethylene glycol; 13) Trinitrite of glycerine.
*By calculation.

The disintegration rate of the hydroxy radical is also increased during complication of a molecule. During disintegration of ethylnitrite this reaction does not play almost any role and in any case the speed of it is immeasurably less than the speed of formation of nitrite from etoxyl and NO [37], during disintegration of n - propyl nitrite it is already very significant [38], and in the case of tert-butylnitrite at 201°, as shows a simple calculation according to the data of Levy [38], the constant of the disintegration rate of tert-butoxyl (k_3) is several hundreds times more, than the constant of speed of formation of nitrite from tert-butoxyl and NO (k_1) (concentrations in mm Hg).

If a molecule of ethylnitrite is complicated, replacing hydrogen of β - carbonic atom not with CH_3, but with ONO, i.e. to turn ethylnitrite into dinitrite of ethylene glycol, then on the initial stage of disintegration this will lead to an increase of speed of breaking the bond O - NO 5 - 6 times more, than upon introduction of a CH_3-group (see Table 3), and also to a certain increase of the disintegration rate of the hydroxyradical, without principal change of the mechanism of this stage.

The very same will occur upon transition from propyl nitrite to trinitrite of glycerine: the main reactions of the initial stage of disintegration will be maintained, but the speed of breaking the bond O - NO and the disintegration rate of the hydroxyradicals considerably will be increased.

If for ethylnitrite the relationships between speeds of main reactions it is possible to present in the form

$$k_1 \gg k_2 \gg k_3,$$

then for glycoldinitrite $k_1 < k_2 < k_3,$

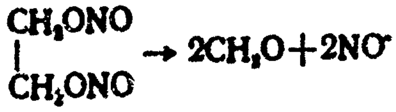
and for glycerine trinitrite, apparently:

$$k_1 \ll k_3 \gg k_2.$$

Upon increase of temperature the relationships between separate speeds of the process obviously change. Disintegration rate of the hydroxyradical is probably triturated faster, than the speed of reactions of its interaction with nitric oxide. This, besides certain indirect data, is indicated by the results of works of American investigators [33], not detecting in the products of disintegration of vicinal dinitrites at 260 - 280° of any organic compounds, besides aldehydes, formed as a result of the breaking the bond between atoms of carbon, and also the results of Pollard's investigations with collaborators

[43], establishing the presence in products of disintegration of ethylnitrate of significant quantities of formaldehyde at ~300° and not finding it at ~200°.

This assumption is confirmed by an experiment with dinitrite of ethylene glycol, conducted by us at 290°. Pressure in this case grew not 2.8 - 3.1 times as in the experiment at 170°, but ~3.8 times, closely approaching to that pressure, which should be created, if the dinitrite is decomposed by the equation



$$\begin{matrix} CH_2ONO \\ | \\ CH_2ONO \end{matrix} \rightarrow 2CH_2O + 2NO$$

The speed of the reaction of disintegration of nitroxyl with an increase of temperature, apparently, also grows somewhat faster, than the recombination rate of the hydroxyradical and NO.

Thus, if one were to consider only initial stages of disintegration, the transition from mononitrites to polynitrites, principal changes in the mechanism of decomposition do not occur. In spite of the fact that this process obviously becomes more complicated, its main regularities remain the same. Naturally, only the speeds of separate main reactions and the relationship between constants of these speeds change, first of all during disintegration of the hydroxyradical and in its reactions with nitric oxide (not in the use of the latter).

However, if we from the initial stages of disintegration turn to consideration of the entire process on the whole, we immediately will encounter an essential, principal distinction of the mechanism of gasphase pyrolysis of polynitrites from mononitrites. It is in the presence of polynitrites in certain conditions of the second self-accelerated and essentially polymolecular stage of disintegration, and also in the appearance in intermediate products of nitrogen peroxide, as it was shown above, closely connected with the degree of development of the self-accelerated reaction.

By analogy with the assumption of American investigators [32], who detected NO_2 in products of disintegration of certain nonvicinal dinitrites near 300° it would have been possible to imagine that nitrogen peroxide appears during disintegration of the hydroxyradical, formed as a result of splitting of one NO-group from a molecule of nitrite. However, apparently, under the conditions of our experiments this reaction plays no part. The main experimental contradiction of the proposal about formation of NO_2 during disintegration of hydroxyradicals is included in the results of experiments with lowering of temperature to the second stage of decomposition of dinitrite of ethylene glycol from 170 to 100°: in spite of the fact that at 100° the speed of thermal disintegration of dinitrite (k) is practically equal to zero, the concentration of NO_2 for a prolonged time (nearly half an hour and more) is increased, and besides the gas phase in the reaction vessel from completely colorless turns into dark-red. Of course any hydroxyradicals, disintegrated with the formation of NO_2, such a picture of the process was not able to be given. Apparently, at the present only with the well-grounded proposal, logically explaining both this fact, and also the totality of remaining experimental data, referring to the second stage of disintegration of polynitrites, is the assumption about the fact that the latter is hydrolyzed on the wall of the vessel in a film covering it with difficulty-volatile products of decomposition. The nitrous acid formed with this is quickly disintegrated with the formation of nitrogen peroxide, which also ensures passage of the reactions of oxidation, yielding organic acids and carbon dioxide detected in the final products.

The assumption concerning the reaction on the second stage of decomposition of polynitrites is well coordinated with the easy hydrolyzing ability of esters of nitrous acid; a well-known phenomenon and long ago described in literature

[24]. The reaction of nitrite hydrolisis can be represented in the form

$$RONO + H_2O \rightleftarrows ROH + HONO$$

and besides the molecule, just as during thermal disintegration, breaks the bond O - NO [18], [19]. This reaction is catalyzed by acid, and the speed of acid hydrolisis, as well as the initial speed of thermal disintegration, upon transition from the lowest members of the series to the highest/is increased [18], [45].

It is possible to consider that in an even larger degree it is increased at transition from mononitrites to polynitrites. This is indicated, for example, by the extremely low stability of the latter at usual temperatures, incompatible with the comparatively small speed of their thermal disintegration at increased temperatures. Indeed, glycoldinitrite almost completely is decomposed upon accumulation in air, being colored dark-green (HNO_2), for the duration of three to six days, glycerinetrinitrite - for the duration of two to three days, whereas ethylnitrite and other mononitrites, inasmuch as it is possible to judge by literary data, can be kept in darkness for a very prolonged time[1].

An analogous picture is observed during the action of water, which decomposes dinitrite of ethylene glycol before the eyes and especially trinitrite of glycerine, but relatively slowly reacts with ethyl - or propyl nitrites.

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[1] Hydrolytic reactions obviously play significant a role also at high-temperature liquid-phase disintegration of esters of nitrous acid. The results of certain, unfortunately not many verified, works on decomposition of nitrites in liquid phase [31], [33] can be easily explained with this assumption.

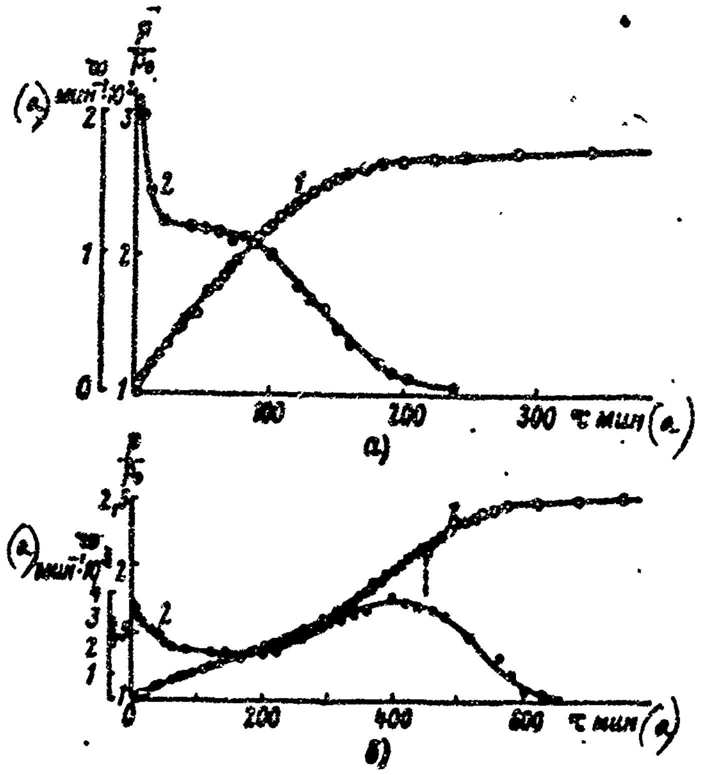

Fig. 28. Disintegration of dinitrite of 1.4 - butyleneglycol.
a - at 170° and p_o = 370 mm Hg, b - at 150° and p_o = 406 mm Hg.
1 - in coordinates $\frac{p}{p_o}$ - τ; 2 - in coordinates w - τ.
(a) minutes.

Obviously, the transition from alkylmononitrites to dinitrite of ethylene glycol and trinitrite of glycerine increases not only and not so much the speed of thermal disintegration, as much the speed of hydrolysis of nitrite.[1] It is possible to consider than an essential role with this is played not only by the increase of quantity of nitrite groups in a molecule, but also by the fact that these groups are located in series with each other. If this last assumption is correct, then the disconnection of nitrite groups in a molecule of polynitrite, for example, by CH_2-groups, has to decrease the role of reactions of the second stage during thermal decomposition of the ester.

---

[1] With this, the introduction of a second nitrite group in a molecule in which there already is one such group, apparently, is more effective, than introduction of a third - ONO group with the two already available.

In order to check the validity of this conclusion, we conducted experiments on disintegration of dinitrite of 1.4-butylene glycol[1]. It turned out that decomposition of this formation at 150 - 190° basically occurs analogous to disintegration of dinitrite of ethylene glycol dinitrite and trinitrite of glycerine with only that difference that at its second stage with the usual initial concentrations of the tested substance in the reaction vessel becomes clearly expressed not at 180°, as in the case of ethylene glycoldinitrite, and only at 150° (see Fig. 28), i.e. its "specific weight" in the process of decomposition is considerably less than during disintegration of ethylene glycoldinitrite[2]. It is necessary especially to emphasize with this that the speed of strictly thermal disintegration of a molecule upon transition from 1.2-ethylene glycoldinitrite to 1.4-butylene glycoldinitrite almost does not change. Let us note also that at 280 - 300° 1.4-butylene glycoldinitrite (in contrast, for example, to 1.3-butylene glycoldinitrite) is decomposed without the formation of NO_2 [32], and, consequently, the possibility of appearance of a second stage due to accumulation of nitrogen peroxide, formed as a result of disintegration of the hydroxyradical, is absent in it.

Esters of Nitric Acid

The results of the above described investigations allow to make certain assumptions concerning the mechanism of thermal disintegration of nitro esters.

The mechanism of thermal disintegration of alkylmononitrates near 200°, based on numerous investigations of pyrolysis of nitro esters the main ones, [3], [17], [27], [35], [36], [41], [42], [43]), of alkylmononitrites

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[1] These experiments were conducted by V. G. Khotin.

[2] It is possible that methylene groups decrease specific gravity of reactions of the second stage of disintegration not only in that case, when they are introduced between ONO groups. Clarity in this question could be introduced by studying the thermal disintegration, for example, of 2, 3-butylene glycol dinitrite.

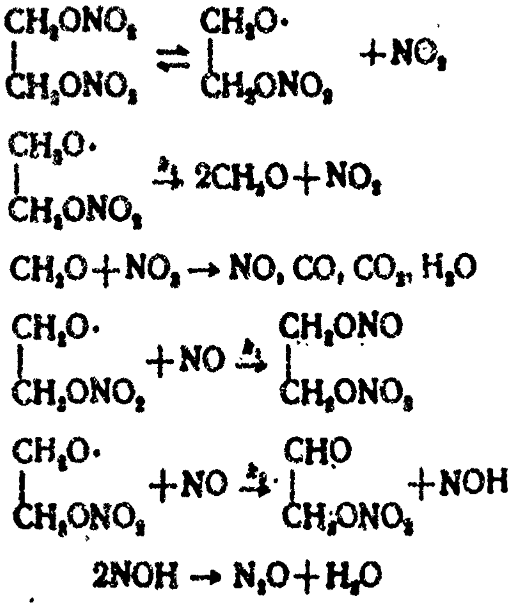
and oxidation of aldehydes by nitrogen peroxide [28], [40] at the present can be represented in the form of the following main reactions [10]:

$$RCH_2ONO_2 \rightleftarrows RCH_2O\cdot + NO_2$$
$$RCH_2O\cdot \rightarrow R\cdot + CH_2O$$
$$RCH_2O\cdot + NO \rightarrow RCH_2ONO$$
$$RCH_2O\cdot + NO \rightarrow RCHO + NOH$$
$$RCHO,\ CH_2O + NO_2 \rightarrow NO,\ CO,\ CO_2,\ H_2O$$

and other products.

$$2NOH \rightarrow N_2O + H_2O.$$

It is possible to assume that, inasmuch as the transition from mononitrites to polynitrites is not accompanied by an essential change of the mechanism of the first stage of disintegration, the main reactions of the initial stages of decomposition of polynitrates also will be analogous to the above mentioned for mononitrate. In the case nitroglycol there could be the following reactions:



$$\begin{matrix} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{matrix} \rightleftarrows \begin{matrix} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{matrix} + NO_2$$

$$\begin{matrix} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{matrix} \rightarrow 2CH_2O + NO_2$$

$$CH_2O + NO_2 \rightarrow NO,\ CO,\ CO_2,\ H_2O$$

$$\begin{matrix} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{matrix} + NO \rightarrow \begin{matrix} CH_2ONO \\ | \\ CH_2ONO_2 \end{matrix}$$

$$\begin{matrix} CH_2O\cdot \\ | \\ CH_2ONO_2 \end{matrix} + NO \rightarrow \begin{matrix} CHO \\ | \\ CH_2ONO_2 \end{matrix} + NOH$$

$$2NOH \rightarrow N_2O + H_2O$$

and so forth.

Based on the results, obtained during the study of disintegration of dinitrite of ethylene glycol, it may be concluded, that the disintegration rate of the hydroxyradical (k_3) in the case of nitroglycol obviously will be larger than in the case of ethyl nitrate, but the relationship of constants of speeds of reactions k_1 and k_2, apparently, will change not in favor of formation of the nitrite-nitrate.

Investigations of thermal disintegration of nitroglycol vapors, conducted in the laboratory of the Moscow Chemical-Technological Institute named after D. I. Mendeleyev [2], [10], [12], [14] and others confirm this mechanism. The disintegration rate, just as in the case of mononitrates, does not depend on initial concentration of nitrate, the activation energy of disintegration (35 - 36 kilocalories mole)is near to the value of it for mononitrates, the gaseous products of disintegration contain NO_2, NO, CO_2, CO, N_2; upon addition of nitric oxide in the products is detected N_2O [10]. During decomposition water formaldehyde and oxalic acid will be formed also. Upon addition of nitric oxide the initial speed of gas formation at 170° decreases (Fig. 29), and besides the character of its dependence on concentration of NO is the same, as during disintegration glycol dinitrite. On subsequent stages of disintegration the addition of NO does not have any influence. At a lower temperature (150°) [14] the addition of NO, just as in the case of decomposition of ethylnitrate in a determined /area/ of conditions [14], [42] does not affect the initial speed of gas formation, but significantly decreases the disintegration rate on the middle stages (Fig. 30).

It is interesting to note that at temperatures below 170° the dependence of speed of gas formation during disintegration of nitroglycol on time has a maximum, the position and magnitude of which do not depend on concentration of nitroglycol [2]. This phenomenon could have been possible to explain by the development of oxidizing reactions, the role of which has to increase by measure of accumulation in products of disintegration of nitrogen peroxide and organic substances.

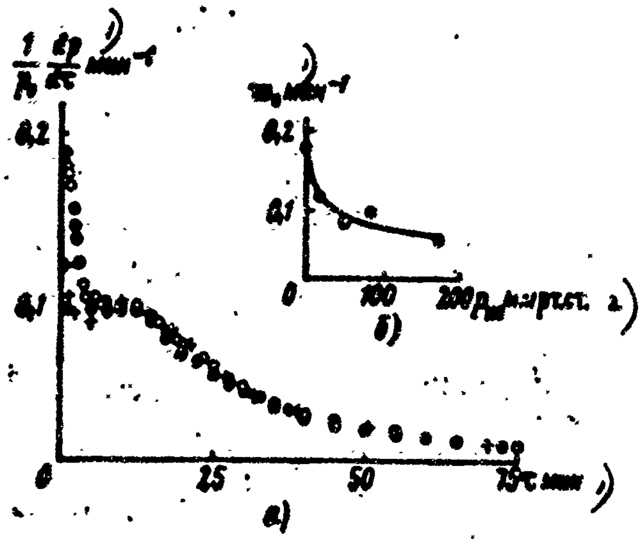


Fig. 29. Influence of NO on disintegration of nitroglycol at 170°
a - change of speed of gas formation in time at p_o (initial concentration of nitroglycol) and p NO: 0 - 157 and 0; + - 196 and 14; ● - 160 and 50 mm Hg.: b - change of initial disintegration rate upon addition of NO.
1) minutes; 2) mm Hg.

However in this case the magnitude and position of the maximum obviously had to depend on initial concentration of nitrate. Inasmuch as such a dependence is not observed, it is possible to assume that acceleration of gas formation is connected with accumulation and subsequent decomposition of intermediate products of disintegration of nitroglycol, for example, nitrate of glycol aldehyde/ or nitrite-nitrate of glycol. In this case the independence of speed of the reaction on concentration of nitrate is more explicable. A decrease of this effect with an increase of temperature and complete disappearance of it at 170° would have been possible to connect with the fact that the role of reactions of formation of saturated mononitrates at a temperature increase decreases and even a greater part of the hydroxyradicals breaks up into formaldehyde and NO_2.

Maybe precisely/ therefore in the case of nitroglycerine, the disintegration rate of the hydroxyradicals of which undoubtedly is significantly higher than nitrate of glyoxyl ($CH_2ONO_2CH_2O\cdot$), the maximum on curve $w = f(\tau)$ during disintegration of NG in vapors is not observed, and the dependence of speed on time for it at all temperatures in the range 140 - 160° is described by curves of the form, depicted in Fig. 29, a[1].

Apparently, in the case of nitroglycerine of reactions, leading to the formation of nitrites, just as other reactions of hydroxyradicals with NO, play still a smaller role, than during disintegration of nitroglycol. Formation of significant quantities of nitrites during disintegration of nitroglycerine and nitroglycol is prevented also by the circumstance that these nitrites are easily decomposed by water, which always will be formed during disintegration of polynitrates.

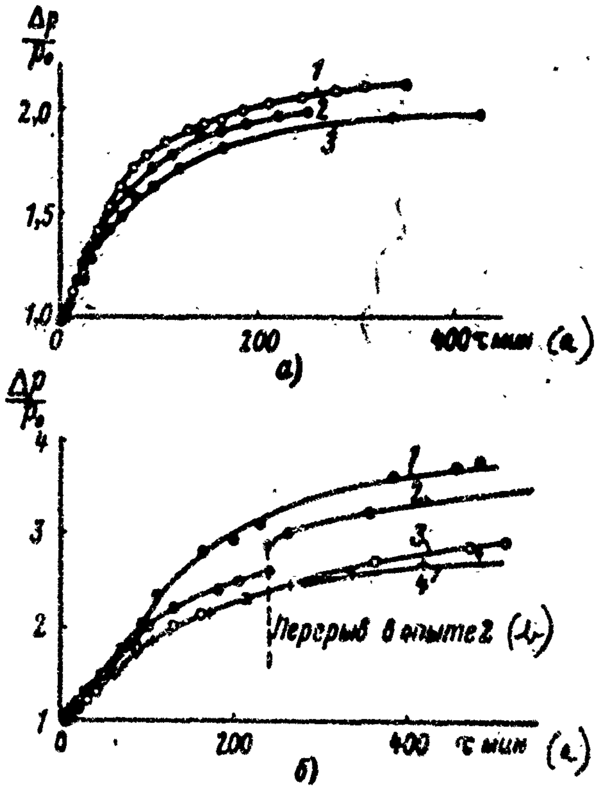


Fig. 30. Influence of nitric oxide on disintegration of ethylnitrate at 181° and nitroglycol at 150° (according to the data of M. S. Plyasunov [14]).
a - ethylnitrate at p_0 (concentration of nitrate) and p_{NO} : 1 - 333 and 0; 2 - 342 and 480; 3 - 247 and 435 mm Hg b - nitroglycol at p_0 and p_{NO} : 1 - 120 and 0; 2 - 116 and 214; 3 - 123 and 631; 4 - 75 and 433 mm Hg. $\Delta p = p - p_{NO}$. (a) min; (b) Break in experiment.

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[1] The absence of a maximum of speed in the case of mononitrates is possible also to explain by the excessively small disintegration rate of alkylmoninitrites —the main intermediate products of decomposition of mononitro esters.

The above-stated considerations are coordinated with results of a recently published paper by Waring, investigating disintegration of nitroglycerine at 140 - 160° with the help of an infrared spectrometer [56]. It was detected that the disintegration rate of vapors of nitroglycerine is subordinated by an equation of a reaction of the first order and decreases in the presence of nitrogen peroxide. No bands of absorption of nitrites in the spectrum of products of disintegration are detected. The displacement of frequencies of the ONO_2-group in the process of disintegration also is not observed; in Waring's opinion, this confirms the great disintegration rate containing a nitrate group of intermediate products. The mechanism of disintegration, offered by this investigator, is analogous to that described above for nitroglycol taking into account the already mentioned changes in speeds of separate reactions.

It is necessary to note that Waring considers the reaction of disintegration of nitroglycerine vapors to be homogenous. This contradicts the results, obtained by other investigators [2], [11], [12]. Some of these results are depicted in Fig. 31 (see [12]). In spite of the fact that the curves, shown in Fig. 31, are obtained by the manometric method, the distinction in speeds of the reactions in vessels without capillaries and with them is so great that to doubt in significant heterogeneity of disintegration of nitroglycerine is hardly possible. Incidentally, disintegration of nitroglycol, as follows for example from Fig. 32, taken from the same work [12], is a considerably homogeneous reaction.

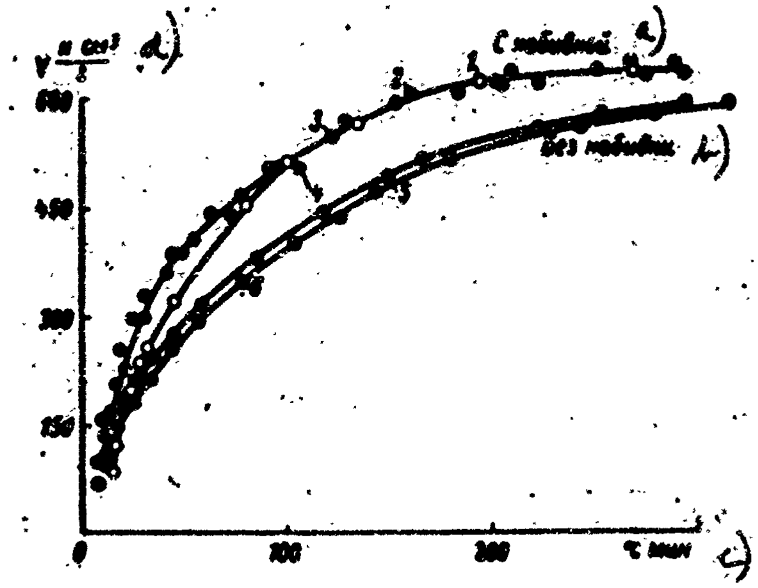

Fig. 31. Influence of filling of the reaction vessel with glass capillaries on disintegration of nitroglycerine vapors at 140° (according to N. A. Mezhevykh [12]).
$(m/v\ g/cm^3)\cdot 10^4$ and s cm^2: 1 - 0.4 and 2000; 2 - 0.5 and 1000; 3 - 0.5 and 1000; 4 - 0.7 and 1000; 5 - 0.5 and 100; 6 - 0.8 and 100. a) With filling; b) Without filling; c) minutes;
d) $V\ \frac{n\ cm^3}{g}$.

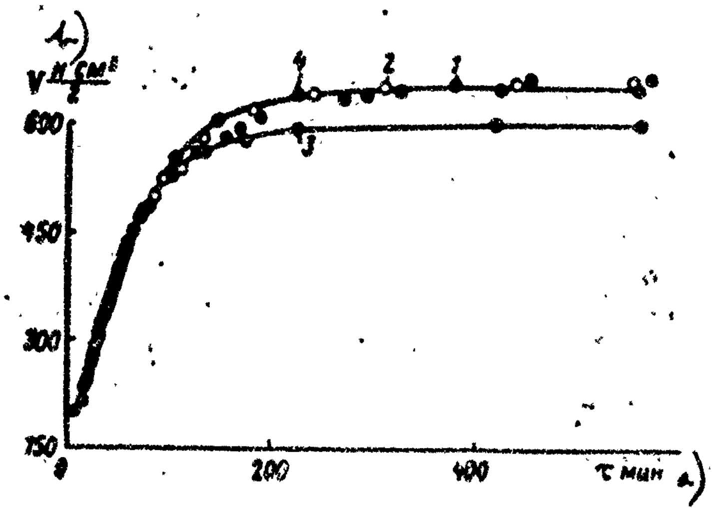

Fig. 32. Influence of surface on disintegration of nitroglycol vapors at 160° (according to N. A. Mezhevykh [12]).
$(m/v\ g/cm^3)\ 10^4$ and s cm^2: 1 - 6.3 and 100 (without filling); 2 - 5.5 and 700 (glass capillaries); 3 - 5.6 and 7000 (glass cotton); 4 - 9.2 and 10,000 (quartz sand).
a) minutes; b) $V\ \frac{n\ cm^3}{g}$.

It is known that during disintegration of polynitrates in liquid phase is great and upon lowering of temperature an ever increasing role is played by hydrolytic reactions. Hydrolysis of polynitrates, just as hydrolysis of nitrites, in the presence of acid is considerably accelerated. It is possible to assume that the speed of hydrolytic reactions and possibly the catalytical action on them of acids is increased upon accumulation in a molecule only of ONO, but also of ONO_2-groups. Their neighboring location may also be especially effective.[1]

It is probable, in a significant degree namely these circumstances, and not an increase, as this still is sometimes considered, the "lability" of the molecule or decrease of activation energy of its disintegration is explained by the essential lowering of chemical stability upon accumulation in a series of nitro esters with an increased number of nitrate groups (upon transition from alkylmononitrates to nitroglycol, nitroglycerine, erythrite tetranitrate and so forth).[2]

Conclusions

Thermal disintegration of alkylmononitrites in the gas phase near 200° was studied by many investigators and represents a relatively simple reaction, the main stages of which are the reversible breaking of the bond O - NO, the interaction of nitric oxide with a hydroxyradical with the formation of a nitroxyl and carbonyl derivative and disintegration of the hydroxyradical.

Gasphase thermal disintegration of dinitrite of ethylene glycol, studied by us at 120 - 190° and initial concentration of 50 - 1000 mm Hg, is more complicated and includes at least two macroscopic stages. The proximity of activation energy of disintegration of this compound to magnitudes, obtained for

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[1] It is necessary to note that the speed of hydrolytic reactions in a number of cases, apparently, can be considerably increased with the accumulation in a molecule of not only nitrites or nitrates, but also nitro groups.

[2] Another important factor, leading to a decrease of chemical stability with an increase of the quantity of ONO_2-groups in a molecule of nitrate, is accumulation during disintegration of nitro esters rich in oxygen of significant quantities of higher oxides and acids of nitrogen, leading to a significant increase of the speed of the reactions of oxidation, the products of which in turn participate in hydrolytic reactions [15].

mononitrites, the influence of nitric oxide on speed, the homogeneity, formation of NO, N_2O and CH_2O and several other facts allow to assume that the mechanism of the first stage of disintegration of this dinitrite is analogous to the mechanism of disintegration mononitrites.

Reactions of the second stage have a self-accelerated in significant degree heterogeneous character and their "specific gravity" considerably increases with an increase of concentration of dinitrite and lowering of temperature of the experiment. The influence of water, containing acid of difficulty-volatile products, the formation of nitrogen peroxide and carbon dioxide and several other facts can be explained, assuming that at the basis of the second stage of disintegration are reactions of hydrolytic character, occurring on the wall of the reaction vessel in a fine film of products condensed on it.

Thus, an increase of the number of ONO-groups in a molecule of nitrite from one to two, comparatively little increasing the speed of thermal disintegration of the molecule, considerably increases the speed of hydrolytic reactions, making them possible even during disintegration of nitrite in vapors at very high temperature.

Trinitrite of glycerine in gas phase at 100 - 160° is decomposed analogous to glycol dinitrite. Disintegration of it is also distage, and the influence of temperature, concentration of nitric oxide, water and condensed products of disintegration, the increase of surface and other factors throughout these stages is satisfactorily described by a diagram, analogous to that, which is offered for glycol dinitrate.

The speed of breaking the bond O-NO in glycerine trinitrite is several times greater than in ethylene glycol dinitrite, and the difference in speeds of reactions of the second stage is even greater.

Certain results of experiments with dinitrite of 1.4 - butylene glycol indicated that the splitting of ONO-groups in polynitrates with CH_2 - groups hardly influences the speed of disintegration, but noticeably decreases the tendency of the process towards self-acceleration, evidently, lowering the speed of reactions of polynitrite with water.

On the basis of results obtained in the study of disintegration of polynitrites, certain conclusions were made with respect to the mechanism of thermal disintegration of nitro esters.

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Chapter 2 Article No. 22

Pages 338-348

Yu. Ya. Maksimov

22. Thermal Disintegration of Vapors of Nitro Derivatives of Benzene

The stability of polynitro compounds of the aromatic series in comparison with explosives of other classes, for example, nitro esters is very great. In connection with this the study of thermal disintegration of nitro compounds until recently was given little attention; any detailed investigations of thermal disintegration, however, are not very numerous, and are in literature only for trinitrotoluene.

Lately in connection with the arising necessity of the petroleum industry for explosives, able for a long time to sustain relatively high temperature, questions of thermal disintegration of nitro compounds took on practical interest.

So that the search of such explosives is conducted more well-grounded, than this was done to this time, it is expedient to establish certain regularities, connecting the peculiarities of thermal disintegration of nitro compounds with their chemical structure and state of aggregation of the substance. As one of the first investigations in this direction there was also a study of thermal disintegration of vapors of nitro derivatives of the simplest aromatic compound of benzene. The results of this investigation are presented in this article.

Experimental Part

Substances and Methodology

Mononitrobenzene. The fraction, liberated from a technical product by means of double distillation in a vacuum. Temperature of hardening is 5.4 - 5.5°, boiling point at 760 mm Hg is 210.5°.

1.3-dinitrobenzene. Technical product was subjected to double recrystallization from acetone and single from methanol. Temperature of melting is 89.5 - 90.0°, boiling point at 760 mm Hg is 300°.

1.3.5-trinitrobenzene. Transparent laminar crystals of greenish shade, obtained with double recrystallization of laboratory product from ethanol. Temperature of melting is 122.0 - 122.5°.

Thermal decomposition of these nitro compounds was studied by the manometric method in a glass vessel of cylindrical form 20 - 25 cm^3 in volume with a glass manometer of the Bourdon type [1]. Residual air pressure in the vessel before the experiment was $10^{-3} \div 10^{-4}$ mm Hg. Decomposition was conducted in a thermostat, filled with liquid tin. Temperature in the thermostat was maintained constant with fluctuations within the limits of ±0.5°. In the process of disintegration the pressure in the vessel was measured. According to these data curves $p = f(\tau)$ were constructed then by graphic differentiation of which the change of the disintegration rate in time was obtained.

Results of Experiments

Mononitrobenzene

The speed of growth of pressure during thermal decomposition of vapors of nitrobenzene decreases in time (fig. 1). The total increase of pressure at the end of disintegration in the range of temperatures 395 - 445°, in which was the most convenient to study decomposition, is 170 - 200% in reference to initial pressure of vapors. Almost from the very beginning of the experiments, on the walls of the reaction vessel a brown deposit will be formed. The intensity of color of which is increased by measure of the course of disintegration. In addition to this, on the later stages of decomposition is observed also precipitation on the bottom of the vessel of a finely-dispersed powder of dark-gray color.

From the data, shown in fig. 1, it is clear that the initial speed of gas formation depends on concentration of the substance (initial pressure). The speed of the reaction at small initial pressures quickly grows with the initial concentration of the substance, and then this growth is delayed. An original influence is rendered by initial pressure of vapors on the character of speed-time curves. At small initial pressures the rate of fall of speed of gas formation diminishes by measure of the course of disintegration. From the beginning and to the end of decomposition the speed in this case decreases according to law of a reaction of the first order.

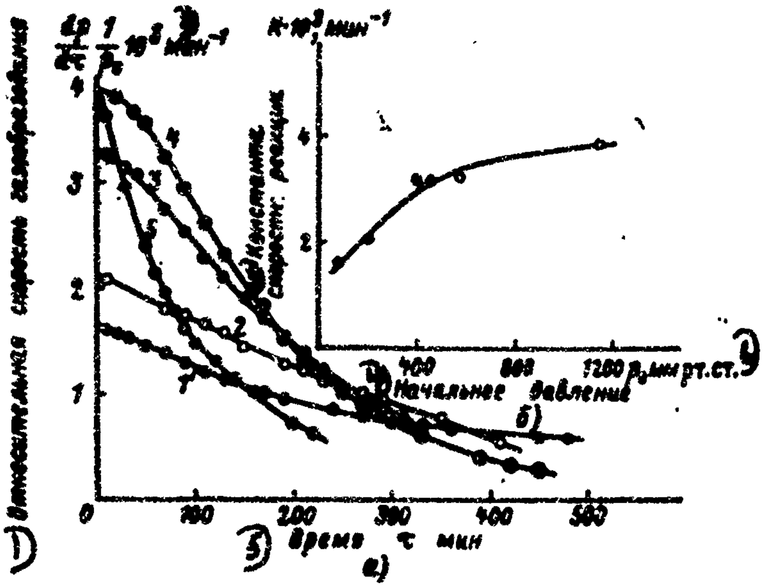

Fig. 1. Thermal disintegration of mononitrobenzene in vapors at 415°.

a) Change of relative velocity of gas formation in time at different initial pressure of nitrobenzene vapors

N curve	1	2	3	4	5
p_0 mm	80	204	575	1150	1000.
s/v cm^{-1}	2	2	2	2	20

Here and further in fig. 2 and 3 s/v - the ratio of total surface of glass to free volume of vessel; p_0 - initial pressure of vapors of nitro compound in mm Hg.

b) Dependence of constant of speed on initial pressure of vapors.

1) Relative speed of gas formation; 2) min; 3) Constant of speed of reaction; 4) Initial pressure; 5) Time τ minutes; 6) p_0 mm Hg.

With an initial pressure of vapors more than 500 mm Hg, the speed of gas formation on the initial stage falls more slowly than on the succeeding one, and on a curve an inflexion point is observed (curves 3 and 4 fig. 1, a).

Proceeding from the assumption that the peculiarities of disintegration of nitrobenzene can be connected with the process of a heterogenous reaction on glass, we conducted experiments, in which the surface of the glass was enlarged by filling the vessel with capillary tubes (curve 5 fig. 1,a).

If, according to the temperature dependence of initial speed of disintegration (angle of incline of initial section of curves p = f (τ)) at a pressure of mononitrobenzene vapors of 400 - 500 mm, E is determined (fig. 4), then the constant of speed, calculated for a reaction of the first order, is expressed by the equation

$$k = 10^{[illegible]} \cdot e^{-\frac{[illegible]}{RT}} \text{ сек.}^{-1}. \qquad (1)$$

Dinitrobenzene

Thermal decomposition of 1.3-dinitrobenzene, studied in the range of temperatures 345 - 410° and with a pressure of vapors of 200 - 800 mm Hg, as can be seen from the curves in fig. 2, occurs with the acceleration of gas formation.

The appearance on a glass surface of brown deposit and dark-gray powder on the bottom of the vessel as a result of disintegration of dinitrobenzene, is qualitatively similar to observations during thermal decomposition of mononitrobenzene. In addition during disintegration of dinitrobenzene, as also of two other nitro compounds of benzene, a certain quantity of products condensed at room temperature will be formed. In all experiments with dinitrobenzene, upon opening the reaction vessel a strong odor of bitter almonds was detected. The total quantity of gases, formed during disintegration, constitutes nearly 3 moles per mole of substance.

Curves p = f (τ), depicted in fig. 2, show that an increase of initial concentration of vapors in two ways affects disintegration. On the one hand, the growth of initial pressure of vapors to a certain limit (at 395° nearly 300 mm Hg) increases the initial speed of gas formation, analogous to the mononitro derivative observed during decomposition. However, the magnitude of maximum pressure in the case of dinitrobenzene is significantly less. On the other hand, an increase of concentration in the entire studied range of pressures leads to a growth of the maximum of speed. The dependence of the maximum speed of gas formation on initial pressure at 395° is well described by the equation .

$$\left(\frac{dp}{d\tau}\right)_{max} = 8{,}83\cdot10^{-4}\cdot p_0^{1{,}36}, \qquad (2)$$

where the speed of growth of pressure is expressed in mm/min. and initial pressure - in mm Hg.

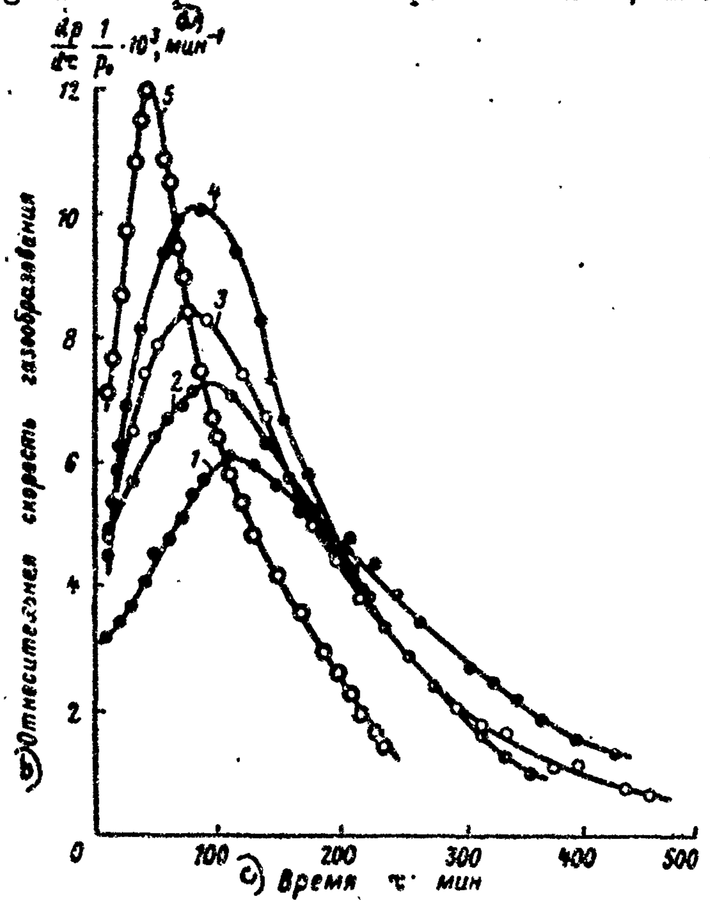

Fig. 2. Change of relative velocity of gas formation in time in the process of decomposition of 1.3-dinitrobenzene in vapors at 395° and different initial pressure.

a) min; b) Relative velocity of gas formation; c) Time minutes.

N curve	1	2	3	4	5
P_o mm	185	307	450	740	665
s/v cm^{-1}	2	2	2	2	20

Increase of the glass surface by 10 times leads in distinction from mononitrobenzene to the growth of speed in the first half of disintegration (curve 5 fig. 2). The maximum of speed in this case is greater, and the stage of its fall occurs earlier, than in experiments without filling the vessel with glass tubes. The pressure of gaseous products in the end of decomposition just as in the case of mononitrobenzene, with an increase of the glass surface becomes noticeably less.

The constant of speed of the reaction of the first order is calculated on the initial stage of disintegration of dinitrobenzene in a studied area of temperatures at a pressure of vapors 550 - 750 mm Hg by the same method as in the case of mononitrobenzene (see fig. 4). The dependence of the constant of speed on temperature is expressed by equation

$$k = 10^{\text{[illegible]}} \cdot e^{-\frac{\text{[illegible]}}{RT}} \text{ сек.}^{-1} \qquad (3)$$

Decrease of the ratio of maximum speed of growth of pressure to initial $\left(\frac{w_{max}}{w_0}\right)$ with an increase of temperature (see table) can be explained by the fact that the speed of secondary reactions depends on temperature in a lesser degree, than the speed of reaction in the beginning of the process. The maximum speed of gas formation is attained independent of the temperature of the experiment at a pressure, constituting 55 - 60% of its final value.

Table

Acceleration of Gas Formation During Decomposition of 1.3-Dinitrobenzene and 1.3.5-Trinitrobenzene Vapors

1) 1,3-динитробензол			2) 1,3,5-тринитробензол		
3) Температура °C	4) Начальное давление паров *мм* рт. ст.	5) Величина ускорения $\frac{w_{max}}{w_0}$	3) Температура °C	4) Начальное давление паров *мм* рт. ст.	5) Величина ускорения, $\frac{w_{max}}{w_0}$
370	548	4,67	312	92	2,24
380	568	3,62	312	137	3,74
395	307	1,62	312	230	6,22
395	450	2,12	312	247	11,4
395	740	2,64	329	193	2,64
410	700	2,33	353	141	1,42

1) 1.3-dinitrobenzene; 2) 1.3.5-trinitrobenzene; 3) Temperature °C; 4) Initial pressure of vapors mm Hg; 5) Magnitude of acceleration

Trinitrobenzene

Decomposition of 1.3.5-trinitrobenzene in vapors was studied in the range of temperatures 270 - 355°. It is characterized by sharply expressed acceleration of gas formation in time (fig. 3). Judging by the intensity of coloring of the walls of the vessel, the total quantity of a substance of brown color, emanating in the form of a deposit on the glass, is small and the dark-gray powder, always existing in products of disintegration of mono- and dinitro-benzene derivatives, in this case was not detected. The quantity of gases in the end of decomposition constitutes 4 - 4.5 moles per mole of trinitrobenzene.

In a wide range of pressures the influence of initial pressure of trinitrobenzene vapors on initial speed of gas formation is not detected.

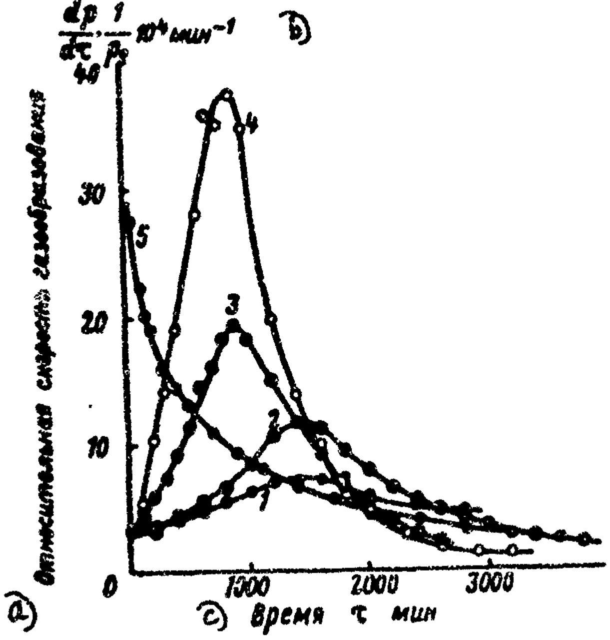

Fig. 3. Change of relative velocity of gas formation in time for decomposition of trinitrobenzene in vapors at 312° and different initial pressure.

a) Relative velocity of gas formation; b) min; c) time τ minutes.

N curve	1	2	3	4	5
p_0 mm	92	137	230	247	135
s/v cm^{-1}	1,5	1,5	1,5	1,5	15

However on the stage of acceleration of the latter, an increase of initial concentration of trinitrobenzene leads to the significant growth of the disintegration rate. At a pressure, not too near to the elasticity of saturated trinitrobenzene vapor, at various temperatures is observed a direct ratio between the maximum of of relative velocity of gas formation and initial pressure of vapors of the studied substance. However upon approach to the pressure of the saturated vapor, the maximum disintegration rate of trinitrobenzene abruptly is increased[1].

In a general case the maximum speed of gas formation is attained in the studied range of temperatures at pressures, constituting 49 - 55% of the final pressures of products of disintegration.

With an increase of the glass surface occurs a sharp increase of the disintegration rate in the initial stage and the character of the curve $p = f(\tau)$ considerably changes. Thus at 312° (fig. 3) an increase of the glass surface by ten times leads to proportional growth of the initial disintegration rate. Further progress of the latter is characterized by a fast monotonous fall of speed up to the end of decomposition.

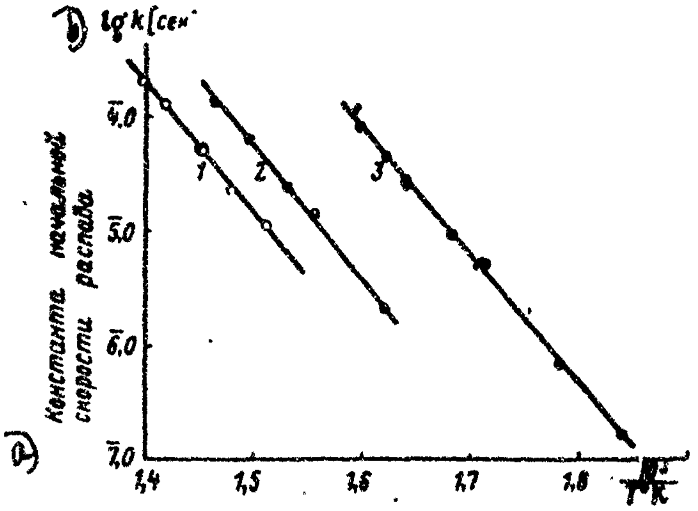

Fig. 4. Dependence of initial disintegration rate on temperature for decomposition of vapors of nitro derivatives of benzene.

1 - Mononitrobenzene, 2 - dinitrobenzene, 3 - trinitrobenzene.

a) Constant of initial disintegration rate; b) log k [sec^{-1}].

The total quantity of gaseous products in this case is 10 - 15% less as compared with experiments without filling the vessel with glass. Application of quartz capillaries and broken glass instead of capillaries did not change the general

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[1] Experiments on decomposition of liquid trinitrobenzene, the results of which will be published separately, show that the disintegration rate of this substance in liquid state is a few times greater, than in vapors.

picture of the phenomenon. Decomposition in a vessel, the walls of which are covered with a deposit of the condensed products of disintegration of trinitrobenzene, did not lead to a change of the initial speed of gas formation.

Determination of the temperature dependence of initial speed of decomposition of trinitrobenzene at s/v - 1 - 2 cm^{-1} (fig. 4) gave speed constants expressed by equation

$$k = 10^{13,40} \cdot e^{-\frac{51900}{RT}} \text{ сек.}^{-1} \tag{4}$$

A decrease with the growth of temperature of the magnitude w_{max}/w_0, the values of which are in the table (see page 342), indicates, as in the case of dinitrobenzene, a weaker, than for the initial reaction, temperature dependence of the speed of secondary reactions, determining disintegration on the stage of acceleration.

Discussion of Results

Thermal decomposition of vapors of mono-, di- and trinitrobenzene side by side with distinctions, stipulated by the peculiarities of chemical structure (number of NO_2-groups in a molecule), has a number of common traits, inherent to the disintegration of compounds, which contain in a molecule the hand C - N. For all three substances the activation energy, determined on the initial stage of decomposition, is practically identical (difference does not exceed the accuracy of determination) and lies within the limits of 51.9 - 53.5 kilocalories mole (fig. 4). The close conformity of the obtained magnitude and measured earlier activation energy of disintegration of nitromethane (53.6 kilocalories mole) [2], [4], indicates the identity of the primary reactions of decomposition of these substances. In turn the activation energy of disintegration of nitromethane is close in magnitude x to the energy of the bond C - N, which according to Cottrell [2], [4] constitutes 52 - 57 kilocalories. This provides a basis to consider that disintegration of nitro compounds occurs namely by the bond C - N[1].

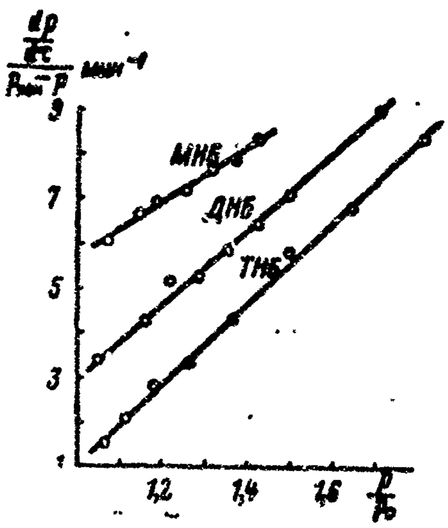

Fig. 5. Check of submission of disintegration of aromatic nitro compounds to autocatalytic law.

1) Condition of experiments; 2) Temperature °C; 3) Initial pressure of vapors mm Hg; 4) Mononitrobenzene (MNB); 5) Dinitrobenzene (DNB); 6) Trinitrobenzene (TNB).

a) min; b) MNB; c) DNB; d) TNB; e) p_{con}.

Another characteristic peculiarity of decomposition of nitro derivatives of benzene is the dependence of the constant of speed of initial reaction of decomposition on the concentration of substance in volume. Significant at low pressure of vapors, this dependence gradually decreases with an increase of pressure. The magnitude of limiting pressure (at which an influence of initial concentration on beginning speed of disintegration already is absent), is sharply decreased with an increase of number of NO_2-groups per molecule. Thus, limiting pressure for disintegration of mononitrobenzene at 415° is approximately 300mm Hg. In decomposition of trinitrobenzene vapors, minimum initial pressure of vapors in the experiments (92 mm Hg) were even higher than the limiting pressure. Explanation of this phenomenon by a change of the mechanism of the monomolecular reaction, as this occurs in an area of small concentrations, when the speed of the process is deter-

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[1] However, later investigation of disintegration of nitroethane and nitropropane indicated that pyrolysis of these nitro compounds occurs not only by breaking the C-N bond. The American investigators, Hillenbrand and Kilpatrick consider that in the disintegration of nitromethane, at least partially, intermolecular regrouping also occurs [5].

mined by the number of collisions between molecules, and the transformation is formally subordinated to bimolecular law, scarcely corresponds to reality. For example, for aliphatic hydrocarbons with a number of carbon atoms in a molecule 1, 2 and 3 pressure of vapors of the substance, with which occurs such a change of the mechanism is significantly less than what was measured for nitro derivatives of benzene and correspondingly equal to 100, 10 and 1 mm Hg. A contradiction of this explanation is given also by the fact that decomposition of mononitrobenzene with small concentration is subordinated to an equation of the first, and not the second order, as could have been expected, if the explanation under consideration was correct.

On the whole, thermal decomposition of nitro compounds is undoubtedly an extremely complex process, including, probably, a large number of elementary reactions[1]. Therefore on the basis of results of only one kinetic investigation, conducted by manometric method, it is impossible to judge the concrete mechanism of disintegration, although they in a known degree also allow to determine the type of complicated reaction. Thus, disintegration of all three studied substances on a significant section (to liberation of gases in a quantity of 50%) follows the autocatalytic law

$$\frac{dx}{d\tau}=k_1(a-x)+k_2x(a-x), \qquad (5)$$

where a - initial quantity of substance, x - quantity of decomposed substance, k_i-constant of speed of monomolecular reaction and k_2-constant of speed of autocatalytic reaction. Fig. 5, in which the results of experiments are represented in coordinates $\frac{\frac{dp}{d\tau}}{p_{\text{кон}}-p} - \frac{p}{p_0}$, shows that the experimental points are well arranged in a

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[1] It is sufficient to say that on the basis of kinetic data and results of analysis of products of disintegration of the simplest nitro compound - nitromethane-- Cottrell with collaborators [4], [5] allow during decomposition of this substance at least 5 reactions.

straight line, as should be according to equation (5). The obtained results are coordinated with the indications available in literature about the autocatalytic nature of decomposition of trinitrotoluene in liquid state [3], [6]. The kinetic law of autocatalysis is observed, as follows from our data, for the duration of a significant share of the period of decomposition and during disintegration of nitro compounds of benzene in gaseous state.

For decomposition of nitro derivatives of benzene in vapors the influence of surface is characteristic. Increase of surface, as show the obtained results, can appear in two ways to influence disintegration. On the one hand, it, in the case of decomposition of di- and trinitro derivatives leads to an increase of the speed of gas formation on the initial stage and, on the other hand, to a decrease of it almost on the entire extent of disintegration.

The accelerating action of a well-developed glass surface on decomposition is developed for various nitro compounds differently. If in the case of mononitrobenzene such an influence practically is absent, then for dinitrobenzene it is already well noticeable, and in the case of trinitrobenzene the initial speed is increased proportional to the increase of the surface of glass. One of the possible causes of the different influence of a glass surface on disintegration of three nitro compounds can be the fact that, due to the distinction in them of boiling temperatures the relative pressure of vapors p_o/p_s[1] (ratio of vapor pressure in the experiment to pressure of saturated vapor) for various substances was different. In experiments with mononitrobenzene the relative pressure did not exceed 0.05, for dinitrobenzene it was nearly 0.1, and in the case of trinitrobenzene 0.5 and more.

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[1] The ratio p_o/p_s can serve as a characteristic of the quantity of a substance, adsorbed on the surface of a solid body.

In this connection one should note the absence of the influence of the chemical nature of the wall on the picture of disintegration of trinitrobenzene. These facts, and also the fact that in liquid state the speed of decomposition of trinitrogenzene is greater, than in vapors[1], indicate that the cause of the accelerating action of the developed surface of glass on decomposition of nitro compounds of benzene in vapors can be the formation on the glass of a liquid film (consisting of a parent substance and the products of its disintegration), in which decomposition occurs significantly faster, than in vapors.

Deceleration of gas formation on subsequent stages of disintegration under the influence of an increase of the surface is conditioned, apparently, by the decrease of total quantity of gaseous products and is connected with the formation on the wall of a deposit rich in carbon. Such an influence of the wall is more sharply expressed in the case of mononitrobenzene and somewhat more weakly during decomposition of trinitrobenzene. An analogous influence of the surface of glass was observed also during decomposition of nitromethane [5]. Explanation of this phenomenon by polymerization on the wall of unsaturated hydrocarbons formed during disintegration, given by Cottrell, is probable and all the more real for compounds of benzene structure, in which there already are unsaturated bonds.

For the duration of thermal decomposition of the three studied nitro derivatives of benzene there is a number of distinctions, conditioned by the peculiarities of their chemical structure. To them refer distinctions in the initial disin-

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[1] An analogous conclusion ensues also from the results of work by A. Robertson, who studied decomposition of trotyl [6]. This phenomenon, probably, inherent to decomposition only of nitro compounds, inasmuch as, for example, in the case of disintegration of alkyl nitrates is observed a reverse influence of the aggregated state [1]. As one of the causes of such an influence of the aggregated state on the speed of decomposition of nitro compounds it is possible to consider the formation of nitrite upon association of an organic radical with NO_2. The formation of a nitrite, distinguished from a nitro compound of significantly lesser stability, takes place most successfully in liquid state, and besides lowering of temperature and increase of pressure promote the progress of the reaction of association in this way [7].

tegration rate, which is increased during transition from mono-to trinitro derivatives. The constant of speed of the reaction is equal to $3.2 \cdot 10^{-5}$ sec.$^{-1}$ for mononitrobenzene at a temperature of 407°, dinitrobenzene - at 397° and trinitrobenzene at 352°. Upon transition from dinitro-to trinitrobenzene the disintegration rate is increased more, than upon transition from a mono- to a dinitro derivative. In connection with the fact that activation energy of the initial reaction of disintegration for all three substances is identical, the change of speed upon transifrom a mono- to a trinitro compound occurs only due to an increase of the pre-exponential multiplier.

In addition, the quantity of nitro groups in a molecule, there is an essential influence on the character of disintegration. If decomposition of mononitrobenzene takes place with deceleration in time, then in the case of a di- and trinitro derivative acceleration is observed, which in the case of trinitrobenzene is expressed greater. The magnitude of acceleration of disintegration, characterized by the relation w_{max}/w_0 during decomposition of both substances is greater, the lower temperature and greater the initial concentration of vapors of the substance. Influence of these factors on the magnitude of acceleration is expressed stronger for trinitrobenzene, than for dinitrobenzene. For the first, lowering of temperature by 40° (from 350° to 310°) leads to an increase of w_{max}/w_0 from 1.5 to 4.5, and an increase of initial pressure leads to the proportional growth of maximum speed; for the second, the same temperature gradient (from 410° to 370°) evokes a change in w_{max}/w_0 from 2.3 to 4.7, and maximum speed increases proportional to the pressure of vapors by 1/3 degree.

Thus, the initial stages of disintegration of the three substances being studied possess identical kinetic characteristics, which indicates, probably, community of the mechanism of reactions on this stage. At the same time, upon transition from mono- to trinitrobenzene is observed an essential change of character of subsequent stages of decomposition. Depending upon the number of nitro groups in a molecule can not only change essentially the relationship of speeds of separate stages of disintegration, but also the very mechanism of the latter. With an increase of the number of nitro groups in a molecule, the reaction ability of the parent substance and intermediate products of the first stage of disintegration (such products can be phenyl, nitrophenyl and dinitrophenyl radicals) is able, apparently, to change unequally. Correspondingly, the introduction of a routine nitro group change the speed of primary and subsequent reactions in different ways. In addition, during decomposition of nitro derivatives of benzene determined and different for mono-, di- and trinitrobenzene, a role, probably, is played also by the oxidizing reactions which are, apparently, one of the main ways of gas formation during disintegration. In favor of that is the fact that upon transition from mono- to trinitrobenzene the total quantity of gases is increased from 1.7 - 2 to 4 - 5 moles per mole of substance.

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Articles No. 23

Pages 349-362

23. Thermal Disintegration of Picric and Styphnic Acids

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Thermal disintegration of picric and styphnic acids is of interest in two aspects.

In certain conditions of industrial application (explosions in deep boreholes) the need appeared for explosives able to sustain for long periods the action of relatively high temperatures. In connection with the fact that nitro compounds of aromatic series are characterized in general by a much lower disintegration rates than explosives of many other classes, the search for heat-resistant substances was begun among them. In order that the search be well-grounded and directed, it was expedient to establish the influence various substitutes in aromatic polynitro compounds on character and speed of thermal disintegration. The study of the disintegration of oxyderivatives of trinitrobenzene--trinitrophenol (TNF) and trinitroresorcin (TNR) was part of the investigations in this art..

Besides this the thermal disintegration of picric and styphnic acids is interesting in comparison with the disintegration of their salts[1] for understanding of the sharp distinction between these salts and acids with respect to speed and

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[1] On the disintegration of salts of picric and styphnic acids--see present collection, page 511.

burning ability.

For salts of a series of metals burning ability is much greater and burning rate is considerably higher than for acids, although the heat of formation of the salts is larger than that of the acids and there is correspondingly less thermal effect of their full transformation during burning or explosion.

Besides, as was shown by recent investigations [2],[4], the dependence of burning rate on pressure for certain picrates and styphnates is unique and is distinguished from the dependence established for the acids.

Inasmuch as during burning one of the stages of the process is decomposition under the influence of heating, it was possible to trust that the comparative study of thermal disintegration of acids and salts would help to explain the cause of the distinction of the characteristics of their burning. This question is considered in the following article, devoted to the thermal disintegration of picrates and styphnates.

Experimental Part

The investigation was conducted by the manometric method in its contemporary variant [1]. A general presentation about the course of the disintegration of both acids is given in Fig. 1. Curves[1] of $V = f(\tau)$ or, which is the same, $p = f(\tau)$ in Fig. 1 and below have a complicated, on the whole S-shaped character. The peculiarities of which will be considered below.

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[1] In order to ease the comparison of results of experiments under various conditions these curves are constructed in coordinates of "volume of gases V n cm^3 at) and 760 mm Hg, formed during decomposition of 1 g substance - in the future n cm^3/g" - "time τ in min". Degree of filling of reaction vessel here and in the future is characterized by the ratio of the sample of explosive (m) to the volume of vessel (v) and is expressed in g/cm^3.

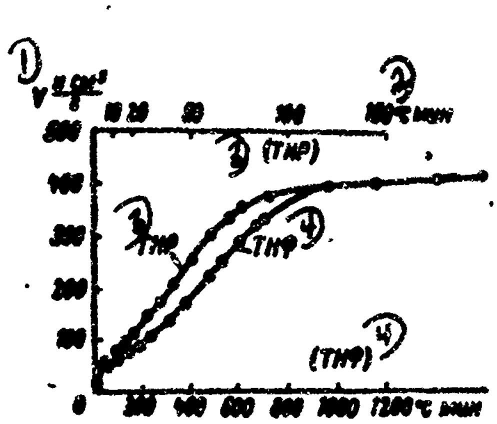

Fig. 1. Comparison of curves of change of specific gas formation in time during decomposition of picric and styphnic acids at 230°. (m/v = $10.45 \cdot 10^{-4}$ g/cm^3 for TNF and $10.50 \cdot 10^{-4}$ g/cm^3 for TNR 1) V n cm^3/g; 2) τ, min; 3) TNR; 4) TNF.

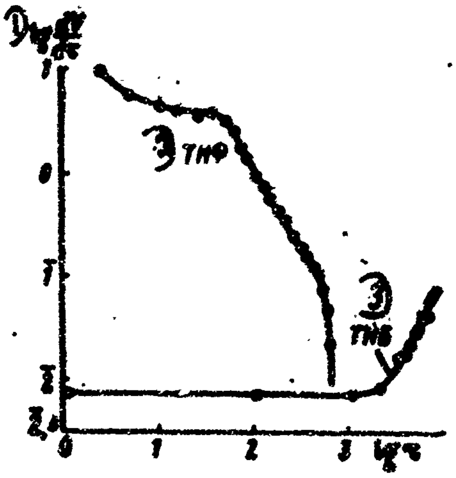

Fig. 2. Comparison of change of rate of gas formation in time during decomposition of picric acid and trinitrobenzene [TB[illegible]] at 270°. (m/v is $12.15 \cdot 10^{-4}$ g/cm^3 for TNF and $29.4 \cdot 10^{-4}$ g/cm^3 for TNB). 1) log (dV/dτ); 2) TNF; 3) TNB.

In Fig. 2 for comparison are shown data for trinitrobenzene (TNB), the slowest to decompose of all studied earlier the trinitro compounds. We see that picric acid is decomposed much faster than trinitrobenzene. The time for achievement of a pressure of gasiform products of disintegration equal to half the maximum (in the future called - "time semi disintegration") constitutes for it at 230° some 470 min, while for trinitrobenzene it equals 218,000 min. General volume of gases formed constitutes for TNF 410 to 450 n cm^3/g or 4.2 - 4.6 moles of gases per mole of explosive.

Styphnic acid is decomposed with the formation of a rather large quantity of gases (440 - 490 n cm^3/g or 4.8 - 5.4 moles per mole of parent substance) and significantly faster (approximately by 10 times)than picric acid. The time of semidisintegration of TNR at 230° constitutes 45 min. At the same time its disintegration rate is many times less than that of the slowest decomposed nitro ester - nitrocellulose. (Time of semidisintegration of the latter at a given temperature, calculated by means of extrapolation is 0.3 minutes, i.e. 150 times less than that for TNR and 1600 times less than that for TNF).

Let us consider now in more detail the conditions under which the experiments were conducted and the results for each of the acids.

Picric Acid

The main experiments were conducted at small m/v ($10 \cdot 10^{-4}$ g/cm^3), allowing to trace the entire course of disintegration, since the final pressure with this does not exceed 760 mm Hg. Results of certain experiments are depicted graphically in Figs. 3 and 4 in coordinates of "time" - "volume" and "time"—"pressure" of gasiform products of disintegration.

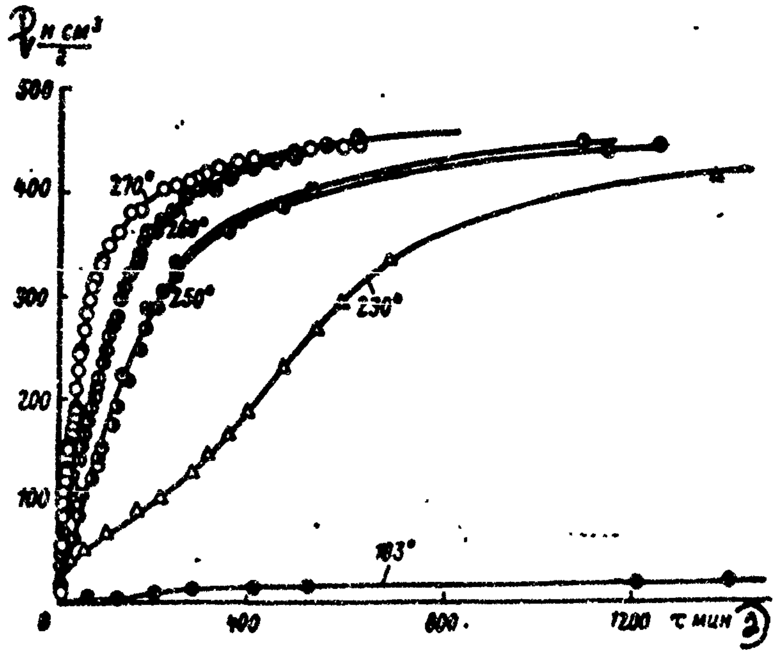

Fig. 3. Change of specific gas formation in time during decomposition of picric acid at various temperatures.
($m/v \approx 10^{-3}$ g/cm^3)
1) V n cm^3/g; 2) τ min.

The path of the curves is unique and indicates the complicated course of decomposition, in which it is possible to distinguish at least 5 stages, differing in the character of the dependence of the rate of gas formation on time.

The first stage, clearly observed at low temperatures and large m/v, is the induction period, during which practically no gas generation is observed. As an example the initial sections of several curves of $p = f(\tau)$, obtained at 183° and various m/v, are shown in Fig. 4. In these conditions induction period can constitute ten of minutes (section OB in Fig. 4).

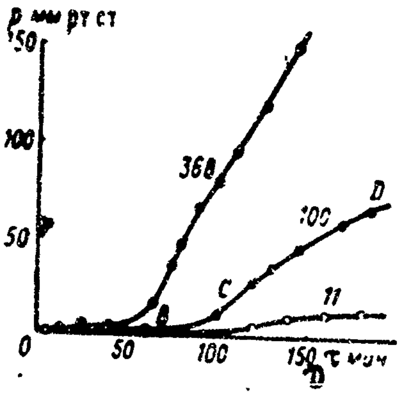

Fig. 4. Initial section of curves of $p = f(\tau)$ during decomposition of picric acid at 183°. (Numbers by curves - m/v in $g/cm^3 \cdot 10^{-4}$). 1) τ min.

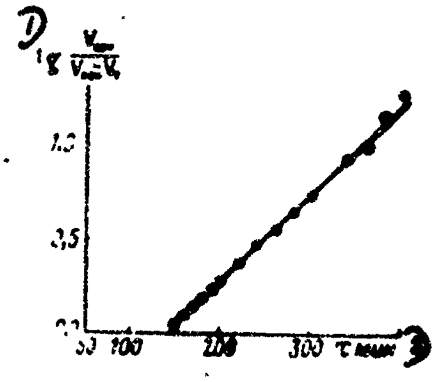

Fig. 5. Check of compliance of disintegration of picric acid on the third stage to the law of reaction of the first order. Experimental conditions $m/v = 11 \cdot 10^{-4}$ g/cm^3, $t° = 183°$. V_{fin} = final volume of gaseous products of decomposition; V_τ = their volume at moment of time τ. (Initial curve shown in Fig. 6). 1) $\log [V_{fin}/(V_{fin} - V\ )]$; 2) τ, min.

If one were to raise the temperature of the experiment by 50° or more, no induction period is detected (Fig. 3). Apparently it decreases so much that it approaches the time of heating of the instrument.

The following stage is the acceleration of gas formation (section BC in Fig. 4), which at 183° lasts about 50 min. On the second stage, apparently, there occurs the development that reaction which proceeds in the induction period, being distinguished from it by the fact that the magnitude of pressure and speed of its buildup increase so much that they become accessible to measurement by the applied method.

Third stage (section CD in Fig. 4) is a fast reaction (average speed of gas generation, for example, at 183° constitutes 0.03 n cm^3/g per min. The speed of of this reaction falls continuously in time according to a law near to that of the course of reactions of the first order (Fig. 5).

The third stage is clearly visible at higher temperatures - up to 250°. Apparently, the temperature dependence of the disintegration rate on this stage is relatively weak. The formed gases, in the main (near 80%), are not condensed at room temperature; the melting temperature of picric acid toward the end of the third stage is lowered only a little (by experimental data, by 0.2° at 183°).

At 183° and small m/v, the rate of gas formation and the quantity of gases formed on the third stage are greater than at large m/v (Fig. 6).

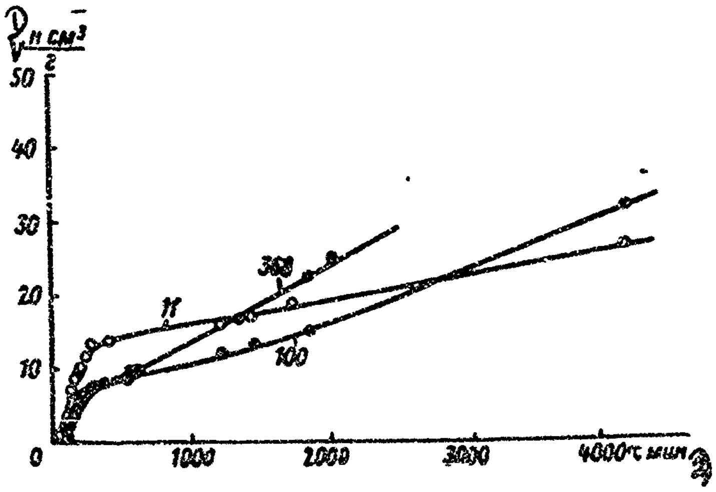

Fig. 6. Influence of m/v on specific gas formation during disintegration of picric acid at 183°. (Numbers by curves - m/v in g/cm^3 $\cdot 10^{-4}$).
1) V n cm^3/g; 2) τ ,min.

Such a dependence on m/v allowed to assume that gaseous products of disintegration (or pressure) retard the development of the given stage of the process. This assumption contradicts however, the results of experiments with a break, when after passage of the third stage the gases were pumped out and the experiment continued. Repetition of the process did not follow, and the following stage began immediately, but proceeded with more than the usual speed (Fig. 7).

Another possible assumption was the consideration of the first three stages of process as sequential stages of development of qualitatively identical reactions with quantitative distinctions in their speed on various stages. The development of the reaction starts immediately, as soon as substance is heated, but proceeds at first so slowly that it is not detected by the mercury manometer (first stage); then follow periods of registered acceleration of gas formation (second stage) and fall of the rate (third stage).

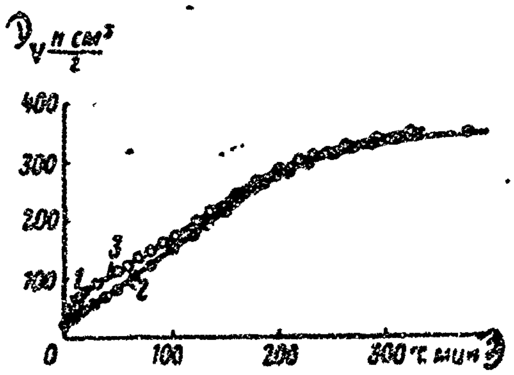

Fig. 7. Influence of evacuation of products of disintegration after initial rise of pressure on subsequent gas formation at $m/v \approx 10 \cdot 10^{-4}$ g/cm^3 and 250°. 1- before evacuation, 2- after evacuation, and 3- parallel experiment without evacuation. a) V n cm^3/g; b) τ, min.

Such a picture was natural in the case of development of autocatalytic or consecutive reactions. It would have been possible to assume also that on the first three stages we are dealing with the decomposition of an unstable impurity contained in the picric acid; however, this assumption would have to be supplemented by the assumption that the impurity is decomposed with self-acceleration. Further, in this case the specific quantity of gases formed would not have to depend on m/v, and in fact, gas formation, as we have seen, considerably decreases during an increase in m/v. Finally, additional purification of TNF did not change the character of the curves, on which, as before, we observed the initial stages of disintegration.

The fourth stage is characterized by a rate of gas formation significantly (3 - 9 times) less than the maximum rate on the third stage, and also on the fourth stage the rate does not fall, as on the third, but grows weakly in time. This growth is expressed the stronger the lower the temperature. Thus at 230°

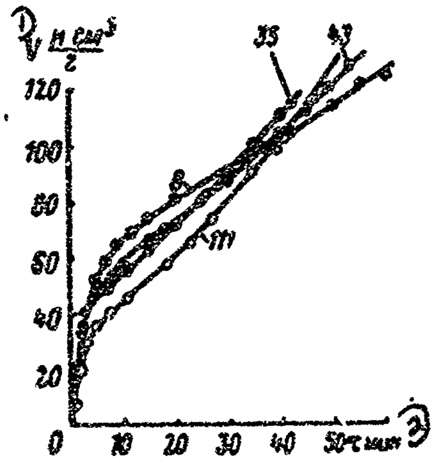

Fig. 8. Influence of m/v on specific gas formation during disintegration of picric acid at 250°. (Numbers by curves - m/v in g/cm^{3} · 10^{-4}). 1) V н cm^{3}/g; 2) τ, min.

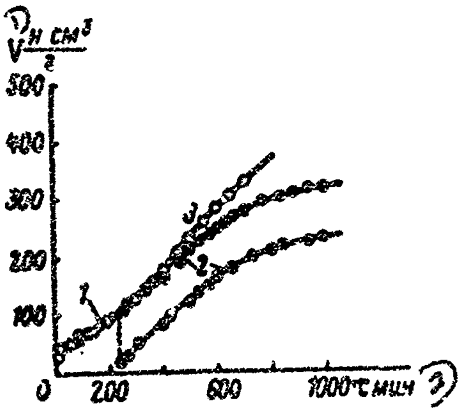

Fig. 9. Influence of evacuation of products of disintegration at the fourth stage on specific gas formation during decomposition of TNF (m/v ≈ 10^{-3} g/cm^{3}, t° = 230°). 1- Prior to evacuation; 2- After evacuation (for convenience of comparison curve is constructed just as a continuation of curve 1); 3- Parallel experiment without evacuation. a) V m cm^{3}/g; b) τ, min.

the maximum rate of gas formation exceeds the initial rate for the fourth stage by 1.9 times, but at 260° by only 6% (in both cases m/v = 10 · 10^{-4} g/cm^{3}).[1]

The rate on the fourth stage also considerably depends on m/v, increasing with it or, which is the same, with a growth in the pressure of gasiform products of disintegration, both at 183° and at 250° (Figs. 6 and 8). At 183° an increase in m/v of 10 times led to an increase in the rate of gas formation of 2 times on the fourth stage.

In order to check the natural assumption that the high rate and large acceleration on fourth stage at increased m/v is caused by the high pressure (concentration) of gasiform products of disintegration, we set up (at 230°) experiments with evacuation of these products on fourth stage, near the maximum of the rate. This [evacuation], however, was virtually not reflected in the magnitude of the rate during continuation of the experiment (Fig. 9), but the

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[1] Comparison is made for rates of specific gas formation, referred to the initial quantity of substance. If one were to refer them to the quantity of undecomposed substance at a given moment, then they will change, naturally, more strongly.

further growth in the rate observed in the usual conditions practically did not occur and on the whole during the period of 400 min the average rate of gas formation after exhausting of gases was 1 1/4 times once less than with exhausting. The same influence is shown by the replacement of gasiform products of disintegration by nitrogen. This speaks of the fact that the process of disintegration is influenced not by pressure as such, but by the chemical nature of the gas producing this pressure.

In order to explain the mechanism of the influence of condensed products of disintegration during its course, we added to picric acid 25% decomposed (volume of gasiform products), fresh acid in the same quantity as was taken for first experiment, and decomposition was continued.

The initial rise in pressure (third stage) was expressed much more weakly; in other respects decomposition proceeded very much like the disintegration of fresh acid at the same m/v. This does not favor the hypothesis of the catalysis of the process by condensed products of disintegration as cause of its acceleration; one should, however, note that acceleration on the whole is expressed relatively of different factors, and in particular of the role of condensed products in the process of disintegration, is hampered.

We will add that the large acceleration of the reaction at low temperatures, usual for autocatalytic processes, speaks for the fact that on the fourth stage we are dealing with reactions having a different temperature dependence - with this the speed of the accelerated reaction depends to a lesser degree on temperature than does a reaction proceeding without acceleration.

Thus as the character of the curve "pressure - time" changes with temperature, the full combination of curves of $p = f(\tau)$ by means of changing the time scale is not obtained. Therefore the determination of the temperature coefficient of the rate was performed by comparison of mean rates at various temperatures on sections of a similar type (fourth stage). In Arrhenius coordinates these speeds give a straight line (Fig. 10).

Finally, it is possible to consider as the fifth stage the period of drop of the absolute rate of gas formation, similar to that which is observed for any reaction as a result of a decrease in the concentration of reagents. This interpretation is supported by an attempt to present the last section of the curve in the usual coordinates of a reaction of the first order (Fig. 11). We see that on a certain, generally small, section the equation of a reaction of the first order is fulfilled with smaller times the rate constant falls, as one should expect. Thus, in essence it may be that one ought to unite the fourth and fifth stages and consider them as two periods of one and the same process, encompassing a reaction whose rate of gas formation is proportional to the available quantity of parent substance, and an autocatalytic reaction whose rate is proportional to the concentration of products of disintegration in simplest case in first degree. Fig. 12 shows that with construction of a graph in coordinates corresponding to the law of autocatalytic reactions, on section where α changes from 17 to 46%, the line of the rate represents a straight line.

Above the course of disintegration of TNF was illustrated mainly by graphs of the change in time of the specific volume of gases formed. The complicated character of the disintegration is still more vividly seen on graphs in the coordinates: "rate of gas formation" — "time" (Fig. 13). In particular, on the curve one can see the presence of two maxima of rate - one corresponding to the end of the second stage and the other being observed on the fourth stage; with this the first maximum is significantly larger than the second; at $m/v = 10.45 \cdot 10^{-4}$ g/cm^3 and 230° the ratio of the rates on the maxima equals 6.85.

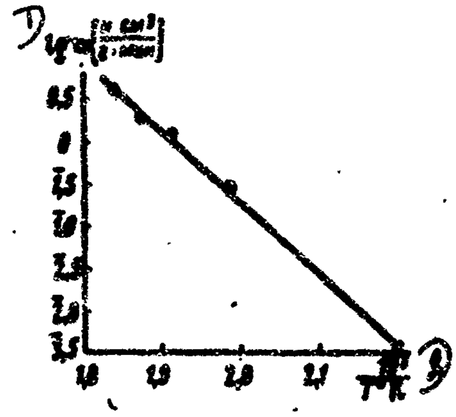

Fig. 10. Temperature dependence of the average rate of gas formation during disintegration of picric acid (fourth stage).
1) log w [n cm^3/g. min]; 2) 10^3/ T, °K.

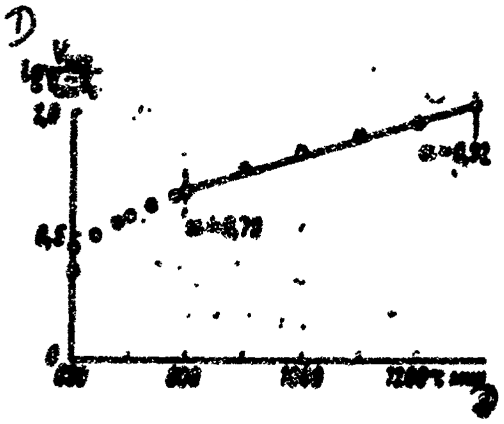

Fig. 11. Check of compliance of disintegration of picric acid on final stage to law of reactions of the first order ($m/v \approx 10^{-3}$ g/cm^3, $t^o = 230°$). α – degree of disintegration = $V\tau/V_{fin}$.
1) log [$V_{fin}/(V_{fin} - V\tau)$]; 2) τ, min.

Besides the above described experiments on the disintegration of liquid picric acid, we conducted experiments on the decomposition of its vapor. The disintegration rate of TNF vapor at 290° is many times less than that in the liquid state. It depends on the initial pressure of the vapor, increasing with at first weakly and then much more strongly (Fig. 14). Simultaneously changes and character of the curve $\frac{dp}{d\tau}\frac{1}{p_0} = f(\tau)$ of describing change in the rate of gas formation with time (Fig. 15). At small pressure of the vapor (30 mm) the curve has a weakly expressed maximum and reaches it late. With an increase in pressure the maximum becomes larger and arrives earlier. With an initial TNF pressure of 110 mm the rate is greatest at the initial moment and drops quickly in time according to a law near to the law of reactions of the first order.

An essential complicating factor is the strong influence of the surface of glass on the reaction of disintegration in the vapor state.[1] An increase of surface by 10 times by means of the introduction into the reaction vessel of

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[1] An analogous phenomenon is observed for other studied nitro compounds (see present collection, page 488).

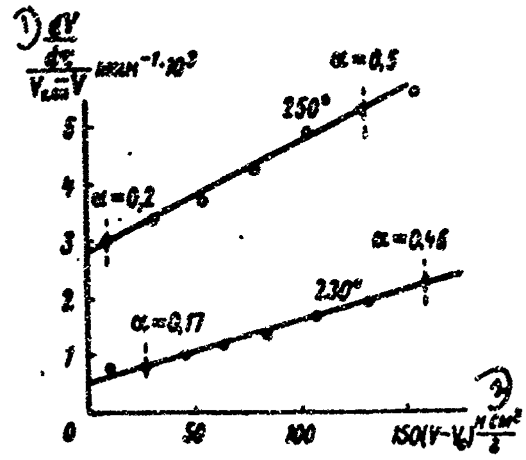

Fig. 12. Check of compliance of disintegration of picric acid to autocatalytic law ($m/v \approx 10^{-3}$ g/cm^3). α - degree of disintegration = $V\tau/V_{fin}$.
1) [$(dV/d\tau)/(V_{fin} - V)$] $min^{-1} \cdot 10^3$; 2) $(V - V_0)$ n cm^3/g.

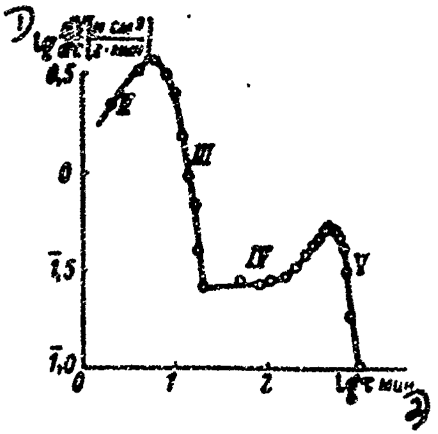

Fig. 13. Change in rate of gas formation in time during disintegration of picric acid ($m/v \approx 10^{-3}$ g/cm^3, $\tau^\circ = 230^\circ$, Roman numerals by curves = stages of disintegration).
1) log $(dV/d\tau)$ [n $cm^3/g \cdot min$]; 2) log τ, min.

glass capillaries increases the initial rate of the reaction by more than 100 times (Fig. 16).

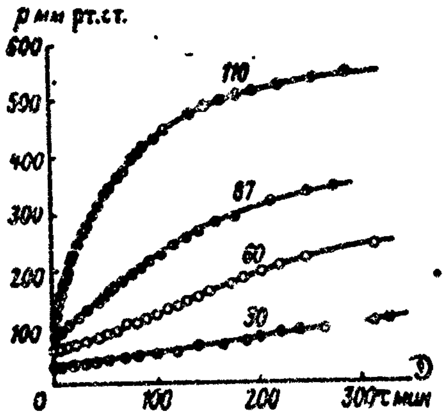

Fig. 14. Growth of pressure in time during disintegration of vapor of picric acid at 290°. (Numbers by curves - initial pressure of vapor of TNF in mm Hg).
1) τ, min.

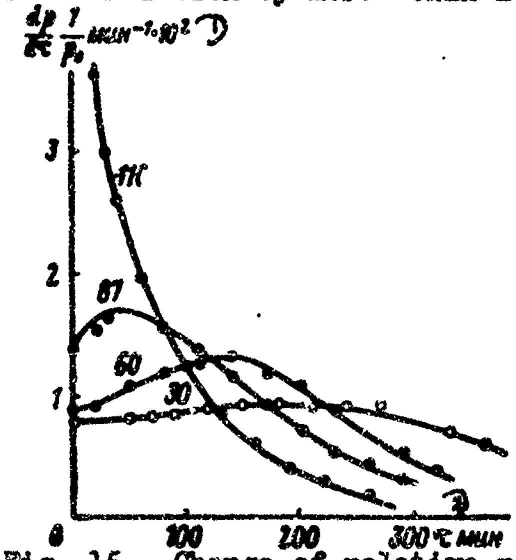

Fig. 15. Change of relative rate of gas formation in time during disintegration of vapor of picric acid at 290°.
(Numbers by curves - initial pressure steam TNF in mm Hg).
1) $(dp/d\tau)$ $(1/P_0)$ min -1 $\cdot 10^2$; 2) τ, min.

It is obvious that the influence of the heterogeneous reaction must be shown considerably also in experiments on the decomposition of the vapor without an artificial increase in the surface, especially, if their pressure is not far from saturation; this in particular can be the cause of strong acceleration of the reaction at p = 110 mm in comparison with p = 87 mm(Fig. 15); acceleration for this reason is possible also in experiments on the disintegration of the liquid at small m/v. Indeed experiments at 230° and m/v $10 \cdot 10^{-4}$ g/cm^3 showed that in a spherical reactionary vessel 6 mm in diameter (s/v - 6.1 cm^{-1}) the rate at the maximum is significantly (1.3 times) greater than with a vessel diameter of 40 mm (s/v = 1.5 cm^{-1}).

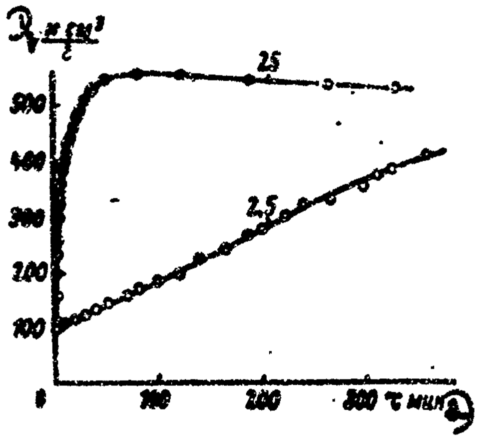

Fig. 16. Influence of filling of vessel with glass capillaries on disintegration of picric acid in the vapor state at 290°. (m/v $2 \cdot 10^{-4}$ g/cm^3, p_0 = 30 mm Hg, numbers by curves - magnitude of ratio in cm^{-1} of the total surface of glass (s) to volume of vessel (v).
1) V n cm^3/g; 2) τ,min.

It is interesting that during decomposition in the vapor state in a vessel with increased surface there will be formed somewhat more gas than without the addition of glass capillaries, but then their pressure slowly falls, obviously as a result of a subsequent reaction proceeding with the formation of condensed products.

Styphnic Acid

A known difficulty in the study of the disintegration of styphnic acid ($\tau^{\circ}_{\text{melt}}$ = 177.5 - 178°) is the fact that it relatively strongly retains water. Evacuation at room temperature and at 100° for two hr is apparently insufficient to remove it. Only evacuation at 180°, when styphnic acid is already in a liquid state, for 5 min excluded fast rise in pressure observed with the regimes given above. This evacuation changes also the character of the initial rise in pressure — from saturable it becomes accelerated. Apparently, the presence of water accelerates primary reactions, which without it are developed more slowly. We speak here of a very small quantity of water, because after 10 min the general quantity of gases in experiments with exhaust at 100° and at 180° becomes almost identical. Fig. 17 illustrates this. A certain influence on the path of the curves is exerted by heating (time of fast growth of pressure constitutes in all about 8 min).

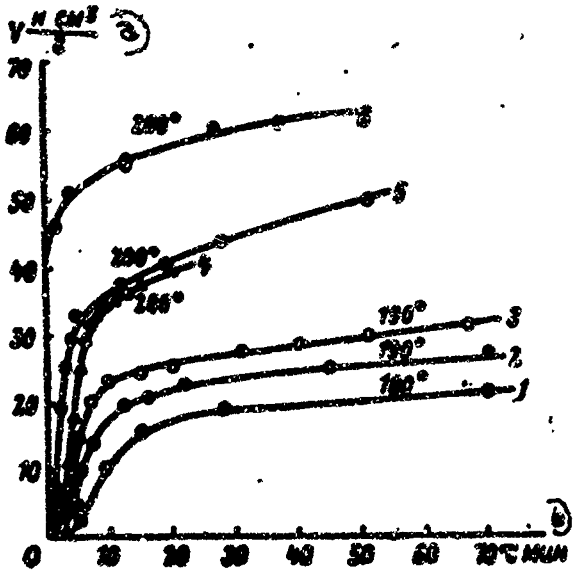

Fig. 17. Influence of conditions of evacuation on disintegration of styphnic acid at various temperatures ($m/v \approx 10 \cdot 10^{-4}$ g/cm^3). Temperature at which evacuation of reaction vessel was conducted: 1- 180°, 2- 100° with liquid nitrogen, 3- 180°, 4- 100°, 5- 100° with liquid nitrogen, 6- 180°. a) V n cm^3/g; b) τ, min..

The general picture of the disintegration of styphnic acid, depicted in Fig. 18, is clear enough and is analogous to that observed for picric acid. It includes a small initial acceleration of gas formation (first stage), decomposition with a significant, but quickly decreasing rate (second stage), section of almost constant, weakly growing rate, (third stage) and finally, its fall (fourth stage).

The first stage is detected only in experiments conducted at the lowest of the studied temperatures: 180°, 190° and 200°. In a certain measure this includes also the second stage, whose duration constituted with these timperatures about 10 minute, with a quantity of gases formed[1] of 20 - 35 n cm^3/g or 0.22 - 0.35 moles per mole of styphnic acid.

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[1] Maximum quantity of gases which can be formed by styphnic acid constitutes by the hypothetical equation
9 1/4 moles per mole or 846 cm^3/g.

With this there will be formed basically gases, not condensed at 0°. We also conducted an experiment on the decomposition of solid styphnic acid at 150°; the pressure fast was lifted rapidly to 46 mm Hg, after which it remained constant for 72 hr.

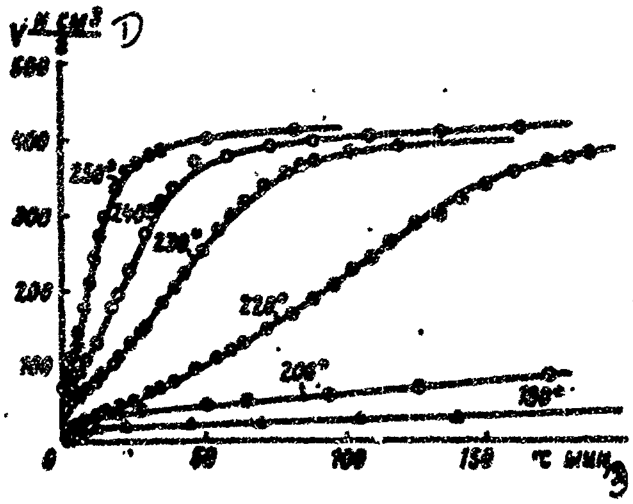

Fig. 18. Disintegration of styphnic acid at various temperatures ($m/v \approx 10^{-3}$ g/cm³). 1) V n cm³/g; 2) τ, min.

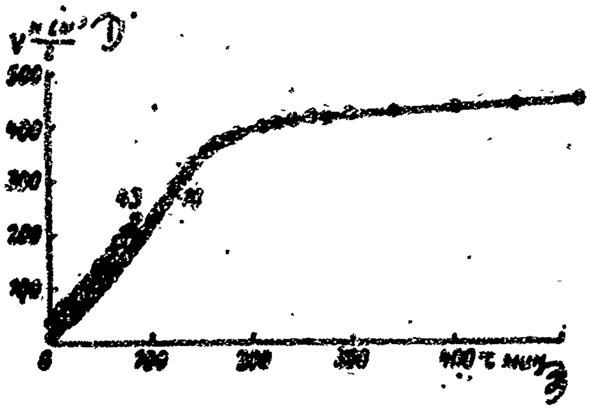

Fig. 19. Influence of m/v on disintegration of styphnic acid at 220°. (Numbers by curves - magnitude of m/v in g/cm³ $\cdot 10^4$). 1) V m cm³/g; 2) τ, min.

This circumstance indicates that the decomposition rate of solid styphic acid is significant less than that of its melt.

The second stage, i. e., section of rapidly falling rate, is shown on graphs of experiments at 220 and 230° (Fig. 18). At 240° and 250° pressure will be raised too fast, so that the section of rate drop could be detected and separated from heating.

Two experiments at 220° were conducted at m/v, differing by 4 times (Fig. 19). At large m/v, gas formation on the second stage was a little greater. Apparently, it grows somewhat also with an increase in temperature, as was shown by comparison of experiments at 190° and 200° (Fig. 17).

The third stage - weakly accelerated gas formation - embraces the main part of disintegration. The rate of gas formation here is much less (6 - 8 times) than on the preceding stage. Small also is the growth of the rate; at 200°

the ratio of maximum and minimum rates constitutes 1.56, at 230° — 1.48, at 240° — 1.42, and at 250° - 120. The rate of gas formation on this stage does not depend on m/v (Fig. 19); the experiments are sufficiently reproducible.

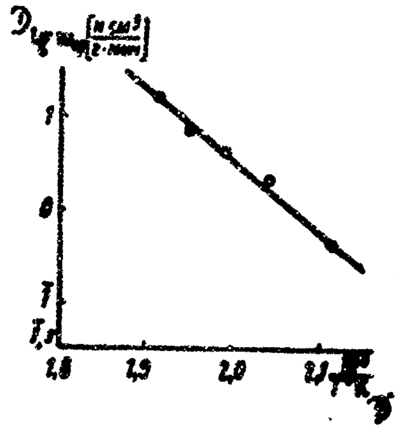

Fig. 20. Temperature dependence of mean rate of gas formation during disintegration of styphnic acid (third stage).
1) $\log W_{av}$ [n cm^3/g·min];
2) $10^3/T$, K.

If the course of the reaction on third stage is expressed by an autocatalytic equation, the relationship for styphnic acid turns out to be twice that of the reaction rate during the disintegration of TNR was determined by comparison of mean rates on the section, where the degree of transformation changes from 22 to 45% (Fig. 20). In Arrhenius coordinates a straight line is obtained. The disintegration rate of styphnic acid at 230 and 250° is approximately 10 times greater than that for picric acid and this difference changes little with temperature.

Discussion of Results

Picric acid is decomposed much faster trinitrobenzene — at 270°, for example, by almost 200 times. However, this circumstance is not its exclusive peculiarity. All substitutes increase the disintegration rate trinitrobenzene. In particular, the disintegration rate of methyltrinitrobenzene — trotyl is of the same order as that of oxytrinitrobenzene — picric acid. The main distinction of the disintegration of picric acid from that of trinitrobenzene and other of its substitutes and the majority of explosives in general, is its very weak (as compared with them) acceleration of disintegration on main section, and even a delay in its course in the beginning of disintegration. The same peculiarity is inherent in styphnic acid, for which it is still more expressed. According to the investigations of Yu. Ya. Maksimov, it is characteristic also for hexanitrodiphenylamine and hexanitrooxanilide, i.e., for all the studied nitro compounds of the aromatic series which contain mobile atom of hydrogen, giving to the compound acid properties.

Another peculiarity of the disintegration of both acids is its clearly expressed phasic character. With this the first stage, encompassing the induction period, the growth of the rate and its fall, proceeds relatively fast and therefore is very noticeable.

The influence of the degree of filling of the vessel, or in other words, the pressure of the gasiform products of disintegration, is developed relatively concerning weakly, especially for styphnic acid. This is confirmed in particular by the opinion expressed earlier that the characteristic which will distinguish nitro compounds of the aromatic series from nitro esters consisted in the fact that for them the acceleration of decomposition is relatively small, and also that it sets in comparatively late. As the vapor, picric acid is decomposed significant more slowly than in the liquid state. This, incidentally, promotes a sharper manifestation of the upper temperature limit of flash, which was established for that substance.

Reaction in the vapor state, as was observed for many other nitro compounds, is strongly accelerated by the surface of glass. This circumstance profoundly complicates the quantitative interpretation of results obtained in glass vessels of other materials.

The dependence of the disintegration rate of picric acid on temperature is small; the average temperature coefficient in the interval 183 - 250°

constitutes (for the main (third) stage of disintegration) 1.12; this corresponds to an activation energy E of 38.6 k-cal/mole and log B of 11.6. For styphnic acid the corresponding values are E = 34.6 k-cal/mole and log B = 11.2. The values we found for E and B for picric acid differ strongly from those listed in the literature [3] (E = 58,000 cal/mole and log B = 22.5). A possible cause of this is the fact that during the calculation of constants the complexity of the kinetic curves was not priviously considered, in consequence of which they compared the reaction rates on section, corresponding to various stages of disintegration -- for example, the induction period at low temperature and the period of fast growth of pressure during increased disintagration. This assumption is favored by the fact that the rate constants calculated by literary data [5] and obtained by us differ much less than their dependence on temperature.[1] One may see also that the pre-exponential multiplier not only does not exceed the usual magnitude for monomolecular reactions,[2] but even more is somewhat lower.

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[1] For the fourth stage, according to Farmer, the rate of gas formation is 0.0070 $cm^3/g \cdot min$, and by our data,. 0.0048 $cm^3/g \cdot min$. Analogously, for the third stage Farmer gives 0.033 $cm^3/g \cdot min$ and our experiments -- 0.041 $cm^3/g \cdot min$. If one considers that m/v may be different (Farmer does not indicate a value for this characteristic). The agreement may be taken to be satisfactory.

[2] We conducted no direct experiments to support the fact that the initial stage of liquid - phase disintegration is a reaction of the first order; there is no basis, however, to expect that picric and styphnic acids are exception in this relation.

Comparison with data obtained by Yu. Ya. Maksimov for trinitrobenzene[1], shows that the distinction noted of disintegration rates of this explosive from that of the acids we studied is basically determined by the significant difference in energies of activation. For trinitrobenzene, according to Maxim, E - 44.0 k-cal/mole and log B - 11.2. If, as is probable, the initial stage of the disintegration a trinitro compound in the benzene ring essentially relieves this breakaway, similar to the way that nitrating.

Conclusions

We studied, with the help of a glass manometer, the disintegration of picric and styphnic acids in the interval of temperatures from 183° to 270°.

This disintegration proceeds in a complicated form and includes a series of stages, distinguished by the character of the dependence of rate on time; on the whole it proceeds without significant acceleration and in this respect is distinguished from the disintegration of trinitrobenzene, trinitrotoluene, and many other nitro compounds of aromatic hydrocarbons.

We determined these kinetic characteristics for the main stage of disintegration; for picric acid $E = 38.6$ k-cal/mole, $B = 10^{11.6}$, "half-life" at 230° - 470 min; for styphnic acid $E = 34.6$ k-cal/mole, $B = 10^{11.2}$, "half-life" at 230° - 45 min. In the vapor state picric acid is decomposed significantly slower than in the liquid phase, and besides side by side with the homogeneous reaction there occurs, with significant speed a heterogeneous reaction on the surface of the glass.

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1. K. K. Andreyev, A. P. Glazkov, N.D. Maurin, and B. S. Svetlov. Journal of Physical Chemistry, 1958, 32, 1726.

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[1] See the present collection, page 478.

2. A. F. Belyayev and A. Ye. Belyayev. Reports of the Academy of Sciences of of the USSR, 1946, 52, 507; A. F. Belyayev and Yu. A. Kondrashkov. Reports of the Academy of Sciences of the USSR, 1960, 131, 364.

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5. Farmer, R. C., J. Chem. Soc., 1920, 117, 1432.

Tape No. 63-254

Article No. 24 Part 1

Pages 363-375

K. K. Andreyev and Liu Pao-feng

24. Thermal Disintegration of Ammonium, Potassium, and Lead Salts of Picric and Styphnic Acids

In distinction from the acids, ammonium, potassium and lead salts of trinitrophenol and trinitroresorcin are not melted and therefore are decomposed at an elevated temperature, remaining in the solid state. Besides, they are nonvolatile and therefore the chemical reaction of decomposition at least in its first stages, proceeds in the solid phase. The known exceptions are the picrate and styphnate of ammonium, which, similarly to other ammonium salts, noticeably dissociate at increased temperatures, as a result of which the decomposition of the vapors of the acids and their interaction with ammonia in the gaseous phase becomes possible.

As is known, salts of picric and styphnic acids (again with the exception ammonium salts) are sharply distinguished in speed and regularities of burning from the acids themselves. One of the problems of the investigation of the thermal disintegration of the salts was to try to detect such of its peculiarities, which would allow to explain the indicated distinctions with respect to burning.

Investigation of the thermal disintegration was conducted by the manometric method with application of a glass manometer of the Bourdon type [1].

In the article we take the following conditional designations:

τ - time in minutes;

V - volume of gases, formed during the decomposition of 1 g of substance, brought to normal conditions $\left(\frac{n\,cm^3}{g}\right)$;

w - speed of gas formation in $\frac{n\,cm^3}{g.min}$;

m/v- degree of filling of reaction vessel in g/cm^3 (m - sample of substance in g, v - volume of vessel in cm^3);

p - pressure of gasiform products of disintegration of substance in mm Hg.

Experimental Part

1. Decomposition of Ammonium Salts of Picric and Styphnic Acids

Picrate of Ammonium

Picrate of ammonium was purified by single recrystallization from hot water. It is not melted during heating, at least, in the interval of temperatures from 200 to 270°, in which we conducted the experiments.

Walls of the reaction vessel at the end of the experiment were covered with a brown deposit, whose intensity increased in the direction toward the bottom of the vessel. Besides this, on the bottom of vessel there remained a loose black powder.

The final volume of gasiform products constitutes 5.6-5.8 moles per mole of picrate (510-530 cm^3/g), i. e., somewhat more than for picric acid (see page 495 of this collection).

The general character of the curves of $V = f(\tau)$ or, which is the same, $p = f(\tau)$ at various temperatures (200-270°) is represented in Fig. 1. We see that, as for picric acid, these curves have an S-shaped character; in the case of the picrate, however, this S-form is more strongly expressed: acceleration of gas formation on first section of the curve-to the inflection point-is significant greater. This can be judged by the data in Table 1, where the ratio of maximum speed of gas formation to its initial value is given for both substances.

A still more graphic distinction can be seen on Figures 2 and 3, where curves of $V = f(\tau)$ for the salt and the acid are compared for two temperatures (230° and 270°).

Table 1

Ratio of maximum speed of gas formation to the initial during the decomposition of picrate of ammonium and picric acid at various temperatures.

$(m/v = (10 \text{ to } 12) \cdot 10^{-4}\ g/cm^3)$

1) Температура °C	2) Пикрат аммония	3) Пикриновая кислота
	4) $w_{max}/w_{нач}$	4) $w_{max}/w_{нач}$
230	17,5	1,9
250	11,7	1,2
260	10,4	1,1
270	5,5	1,0

(1) Temperature, °C;(2)Picrate of ammonium; (3) Picric acid; (4) w_{max}/w_{init}.

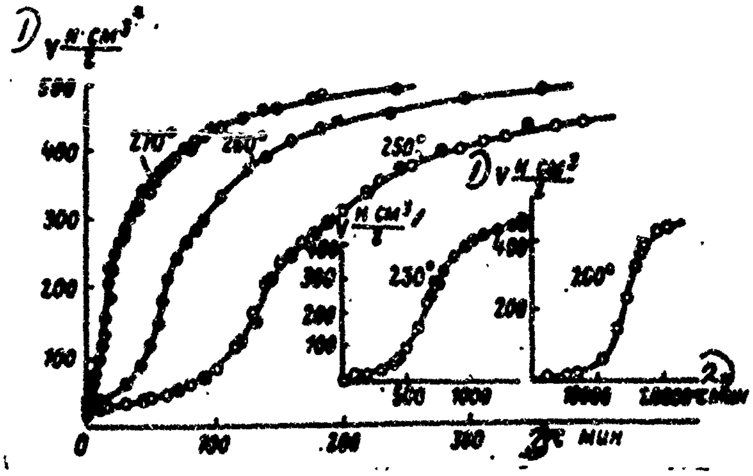

Fig. 1. Disintegration of picrate of ammonium at various temperatures $(m/v \approx 10^{-3}\ g/cm^3)$. (1) V $\frac{n\_cm^3}{g}$; (2) τ , min.

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In the initial stages of disintegration the decomposition rate of picrate of ammonium is less than that of picric acid, but it grows in time significantly faster. At low temperatures (230°) the curve of $V = f(\tau)$ of the picrate proceeds on almost all its extent lower than the curve for the acid and crosses the latter only when V is close to 400 n cm^3/g. Within increase in temperature the initial disintegration rate of the picrate grows more strongly than that of the acid, and, although its acceleration of disintegration in time decreases with a growth in temperature, the intersection of curves of $V = f(\tau)$ occurs earlier; at 250°, when $p = \frac{1}{2} p_{fin}$, and at 270°, when $p = i\, p_{fin}$.

Another peculiarity of the manometric curve of the decomposition of picrate of ammonium is its clearly expressed diphasic character, expresesed in the given case by the fact that after achievement of degree of decomposition of about 50%, the rate of gas formation immediately strongly by 2-5 times decreases and its growth abruptly changes to a slow drop.

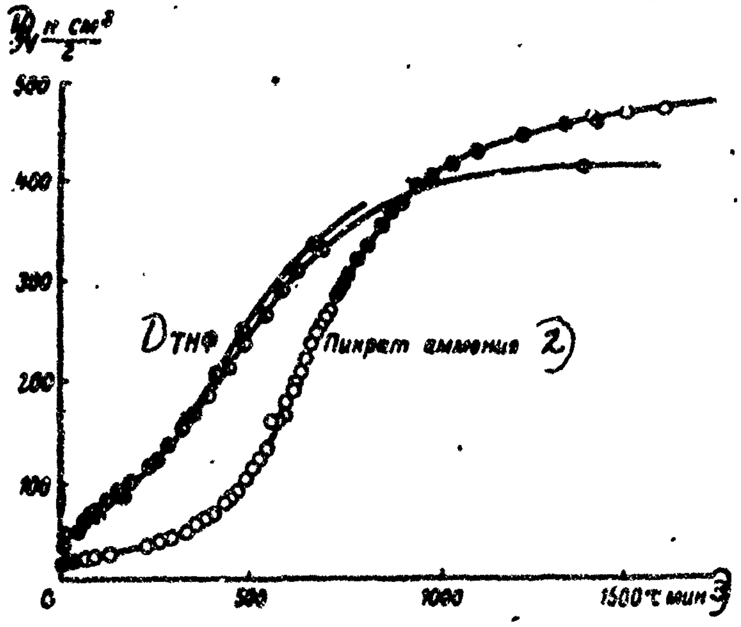

Fig. 2. Comparison of curves of gas formation during the disintegration of picric acid (TNF) and picrate of ammonium at 230° ($m/v \approx 10^{-3}$ g/cm^3). (1) TNF; (2) Picrate of ammonium; (3) τ, min; (4) $V \frac{n\ cm^3}{g}$.

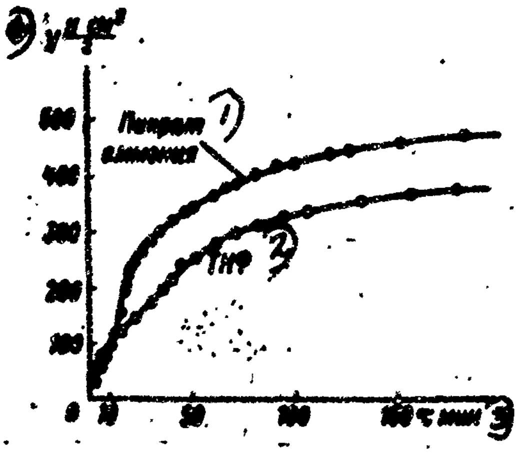

Fig. 3. Comparison of curves of gas formation during the disintegration of picric acid (TNF) and picrate of ammonium at 270° ($m/v \approx 10^{-3}$ g/cm^3). (1) Picrate of ammonium; (2) TNF; (3) τ, min; (4) $V\frac{n\ cm^3}{g}$.

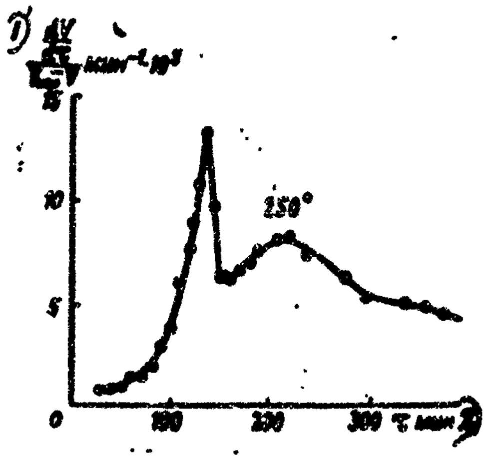

Fig. 4. Change of relative rate of gas formation in time during the disintegration of picrate of ammonium ($m/v \approx 10^{-3}$ g/cm^3). (1)$(dV/d\tau)/(V_{fin} - V)$ min^{-1}.10^3; (2) τ, min.

This change of the law of variation of the rate of gas formation is clearly visible even on integral graphs, especially at 230°-260°; it is still more graphically revealed on differential curves, if on the axis of the ordinates we plot not the absolute, but the relative rate, i. e., the ratio of reaction rate to the quantity of unreacted substance (Fig. 4); in this case it is clear that there occurs not only a drop in the rate, but also a subsequent growth of its relative value, i. e., that curve $w_{rel} = f(\tau)$ has two maxima, and besides the first of them is significantly larger.

The dependence of disintegration rate on temperature was determined by the construction of an arrhenius graph for the initial speed in the interval from 200 to 270°. Points are satisfactorily plotted on a straight line (Fig. 5, line 1), along the tangent of the angle of inclination which gives an activation energy E of 57.2 kcal/mole; since the absolute value of the rate of gas formation is relatively great ($k\ 200 = 2.9 \cdot 10^{-8}$ sec^{-1}), then a correspondingly large pre-exponential multiplier B ($\sim 10^{19}$) is obtained.

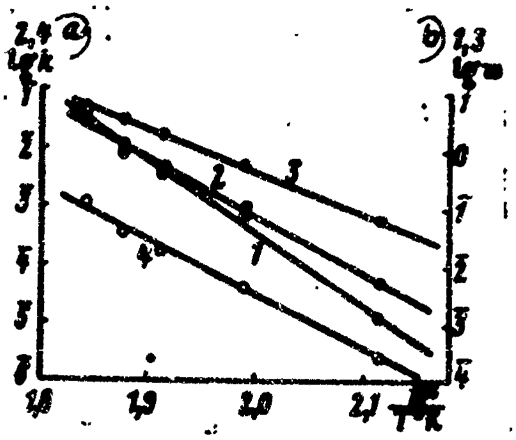

Fig. 5. Temperature dependence of rate of gas formation during disintegration of picrate of ammonium. (1) by initial rates of gas formation; (2) by average relative rate of gas formation; (3) by rate of gas formation in beginning of second stage; (4) by the value of the constant decomposition rate; (a) 2.4 log k; (b) 1.3 log w.

The strong dependence of the initial disintegration rate of picrate of ammonium on temperature, significantly larger than for picric acid, leads to the fact that at high temperatures it is decomposed, on the average, faster than picric acid, and at low temperatures, slower.

The growth in the initial rate in the given case turns out to be more essential than the decrease of acceleration with an increase in temperature. In agreement with this are the results of the determination of the temperature dependence of the average rate of gas formation (on section of change of the degree of disintegration from 3 to 11 to 45%), giving E = 43 kcal/mole (Fig. 5, line 2). The fact that the temperature dependence of the average rate turns out to be less than that for the initial naturally is explained by the high acceleration of disintegration at low temperatures.

As it was shown, the decomposition of picrate of ammonium proceeds in two phases. The rate in the second stage naturally also increases with temperature, although more weakly than in the first. Therefore the ratio of the maximum disintegration rate in the first stage to the initial rate in the second increases with an increase in temperature (see Table 2).

Table 2

Rate of gas formation in different stages of the disintegration of picrate of ammonium (m/v = 10 to 12)· 10^{-4} g/cm^3).

1) Температура °C	2) $(w_{макс})_1$ в см³/г·мин	3) $(w_{нач})_2$ в см³/г·мин	4) $\frac{(w_{макс})_1}{(w_{нач})_2}$
200	0,009	—	—
220	0,98	0,54	1,8
250	4,2	1,7	2,5
260	9,1	3,1	2,9
270	21,7	4,8	4,5

(1) Temperature, °C; (2) $(w_{max})_1$ n cm^3/g•min; (3) $(w_{init})_2$ n cm^3/g·min; (4) $(w_{max})_1 / (w_{init})_2$.

If the initial rates of the second stage at various temperatures are plotted on a graph in arrhenius coordinates, we also obtain a straight line which gives E = 32.2 kcal/mole (Fig. 5, line 3).

Change of disintegration rate in time. The growth of the rate of gas formation in time is significantly stronger at low temperatures than at high; therefore a change in the time scale does not succeed in combining curves of $V = f(\tau)$.

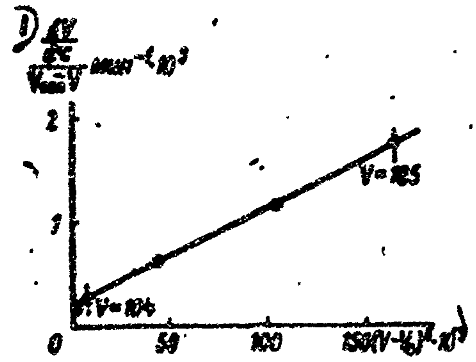

Fig. 6. Check of the compliance of the first stage of the disintegration of picrate of ammonium at 200° to the autocatalytic law. (1) $(dV/d\tau)/ V_{fin} - V)$ min^{-1}. 10^3.

During the construction of the dependence $w = f(\tau)$ in logarithmic coordinates, a straight line is not obtained.

Construction of a graph on the basis of the equation of the autocatalytic reaction

$$\frac{dx}{d\tau} = k_1(a-x) + k_2x^n(a-x)$$

allows us to describe a significant part of first stage disintegration at 200-250°, but for $n > 1$ and other values for various temperatures ($n = 5$ for 200°, 230°, 250° and $n = 3$ for 270°). In Fig. 6 is presented a corresponding graph, characterizing the first stage of disintegration of picrate of ammonium at 200°.

A good approximation to a straight line is given by the construction of experimental data in the coordinates $\log (V - V_0) = f(\tau)$, where V_0 is near to that volume which corresponds to the initial pressure, appearing during heating of picrate of ammonium to the temperature of the experiment. In the interval, where from 3-13 to 40% gasiform products will be formed (i. e. from 14-70 to

210 n cm^3/g) we obtain a straight line (Fig. 7). Calculation of the dependence of the tangent of the angle of inclination of the line on temperature gives E = 40.5 kcal/mole (Fig. 5, line 4), not far from the value obtained for average rates.

The influence of the degree of filling of vessel (w/v) on flow of disintegration. At 250° and 270° the magnitude of m/v relatively weakly affects the course of disintegration; an increase in m/v decreases the initial rate of gas formation, but the growth of the rate goes faster and its maximum is greater. An increase in m/v increases the rate of gas formation also on the second stage of disintegration (see Fig. 8).

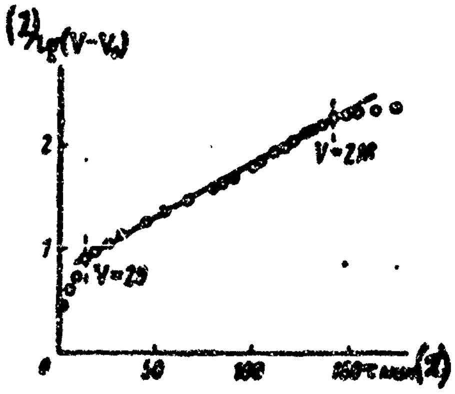

Fig. 7. Straightening of curve of V = $f(\tau)$ of the decomposition of picrate of ammonium at 250° (m/v ≈ 10^{-3} g/cm^3, V_0 taken equal to 21 n cm^3/g). (1) log (V - V_0); (2) τ, min.

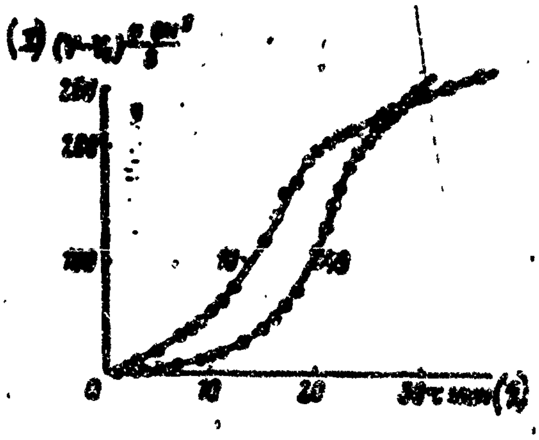

Fig. 8. Influence of m/v on gas formation during the disintegration of picrate of ammonium at 270°. (Numbers by the curves - m/v in $g/cm^3 \cdot 10^{-4}$). (1) (V - V_0) $\frac{n\ cm^3}{g}$; (2) τ, min.

Styphnate of Ammonium

Styphnate of ammonium was obtained from a hot (80°) saturated solution of styphnic acid (m.p. - 178°) by neutralization by a 25% surplus solution of ammonia. During cooling falled orange crystals of styphnate of ammonium were precipitated. The product was purified by recrystallization from hot water.

The final volume of gasiform products of disintegration constitutes 6.2 - 6.7 moles per mole of styphnate (500 -540 n cm^3/g).

The external picture and general character of the decomposition of styphnate of ammonium is similar with that of picrate (Fig. 9).

In the first stage of disintegration we observed acceleration of gas formation (secton AB in Fig. 9); after achievement of a pressure constituting about 40% of the final, the speed of gas formation drops sharply (by 5-6 times), and then starts anew to grow (secton BC). Thus, in distinction from picrate of ammonium, the growth in the disintegration rate in the second stage is expressed more strongly -- not only relative but also absolute velocity is increased. This general character of the curve of $V = f(\tau)$ or, which is the same, $p = f(\tau)$, is observed in all the studied intervals of temperatures, but at the lowest of them (190°) there is no growth of absolute velocity in the second stage - it remains constant for a long time.

At 190 and 200° the curve of $p = f(\tau)$ for styphnate of ammonium in its entire extent lies below the corresponding curve for styphnic acid (Fig. 10). With an increase in temperature the distinction in the disintegration rates of styphnate of ammonium and styphnic acid decreases and at 230° their average rates of decomposition already becomes close (Fig. 11).

The presence of two maxima of **disintegration** rate can be more clearly seen on a differential curve (Fig. 12); with a lowering of temperature the relative magnitude of the second maximum becomes less and at 190° it disappears.

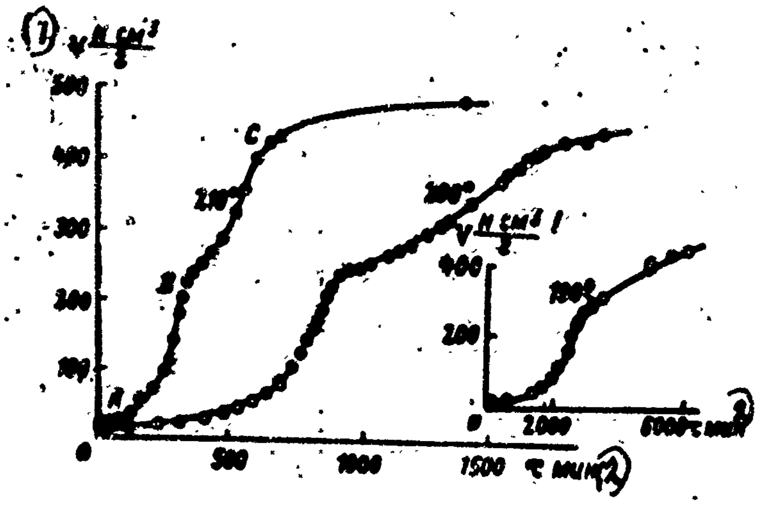

Fig. 9. Disintegration of styphnate of ammonium at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) $V\frac{n\ cm^3}{g}$; (2) τ, min.

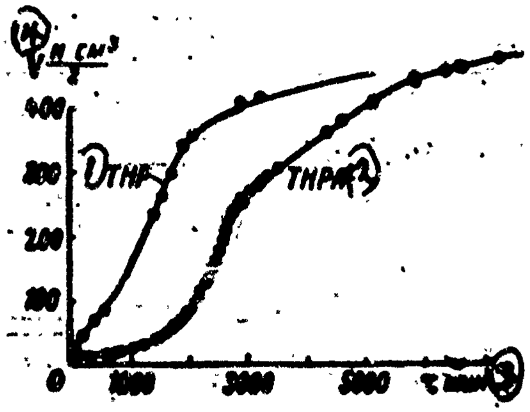

Fig. 10. Comparison of curves of gas formation during the disintegration of styphnic acid (TNR) and styphnate of ammonium (TNRA) at 190° ($m/v = 10^{-3}$ g/cm^3). (1) TNR; (2) TNRA; (3) τ, min; (4) $V\frac{n\ cm^3}{g}$.

Dependence of disintegration rate on temperature. Combination of the curves of $V = f(\tau)$ at the stage of the first acceleration does not give satisfactory results; as for picrate of ammonium the rate of gas formation grows-in time more strongly at low temperature, than at high. Construction of the initial speeds in arrhenius coordinates gives a straight line, along the tangent of whose angle of inclination E = 56 kcal/mole (Fig. 13, line 1). If for a base for that construction we take the average rate of the section, where from 2-9 to 45% of the final volume of gases will emanate, the activation energy obtained is somewhat less: 45.5 kcal/mole (Fig. 13, line 2). Almost the same value is given by construction of the dependence on temperature of the coefficient with a τ of the model equation for the rate. With this the construction, the experimental values of the rate were corrected by substraction of the initial value of w_0, obtained by extrapolation of the curve $w - \tau$ for a time, equal to zero.

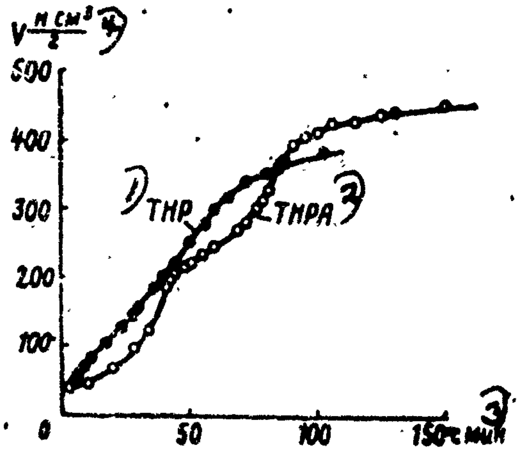

Fig. 11. Comparison of curves of gas formation during the disintegration of styphnic acid (TNR) and styphnate of ammonium (TNRA) at 230° ($m/v \approx 10^{-3}$ g/cm^3). (1) TNR; (2) TNRA; (3) τ, min; (4) $V\,\frac{n\ cm^3}{g}$.

In Table 3 are given the ratios of the maximum rate to the initial for both stages of the disintegration of the styphnate at various temperatures; for comparison the corresponding data on the disintegration of styphnic acid are given also. The data of the table show that, as for picrate of ammonium, in the first stage the growth of the disintegration rate of the styphnate is the greater the lower is the temperature, and for the second stage the acceleration is the less, the lower is the temperature; at 190° (if one were to compare absolute velocity) it is practically absent.

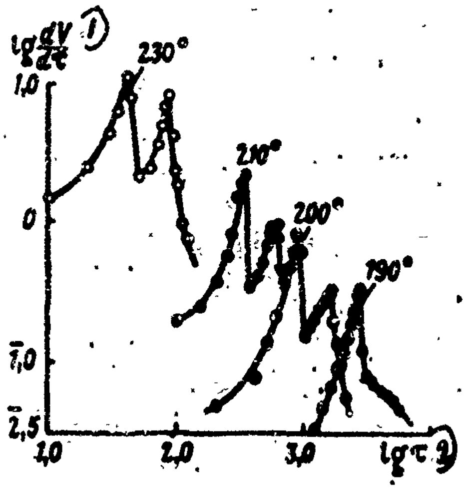

Fig. 12. Change in the rate of gas formation in time during the disintegration of styphnate of ammonium at various temperatures. (1) log (dV/d τ; (2) log τ .

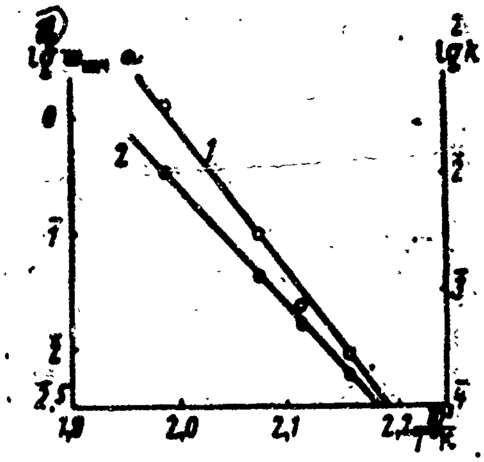

Fig. 13. Temperature dependence of the rate of gas formation during the disintegration of styphnate of ammonium. (1) by initial rate of gas formation; (2) by average relative rate of gas formation on the first stage. (a) log w $_{\text{init}}$.

The dependence of the rate of reaction on temperature for the second stage was determined by the combination of the curves p = f (τ) at 210-230°. Construction of the dependence of the coefficient of combination on temperature in arrhenius coordinates gave E = 48.1 kcal/mole. In connection with the fact that the curve of p = f (τ) for 190° no longer can be combined with the curves of gas formation at higher temperatures, the temperature dependence of the disintegration rate of styphnate of ammonium was also calculated proceeding from the initial rates of the second stage; in this case E is obtained equal to 40.2 kcal/mole.

Table 3

Ratio of the maximum rate of gas formation to the initial for two stages of the disintegration of styphnate of ammonium (m/v = (9.4 to 10.7) 10^{-4} g/cm^3).

(1) Температура °C	(2) Стифнат аммония		Стифниновая кислота
	(4) $\left(\frac{w_{max}}{w_{нач}}\right)_1$	(4) $\left(\frac{w_{max}}{w_{нач}}\right)_2$	(4) $\frac{w_{max}}{w_{нач}}$
190	38	1,0	1,6
200	34	2,0	1,6
210	21	2,3	—
230	8,7	3,7	1,5

(1) Temperature, °C; (2) Styphnate of ammonium; (3) Styphnic acid; (4) $\frac{w\ max}{w\ init}$.

Thus, as for picrate of ammonium, the rate of the second stage of the disintegration of the styphnate depends significantly more weakly on temperature than does the rate of the first stage.

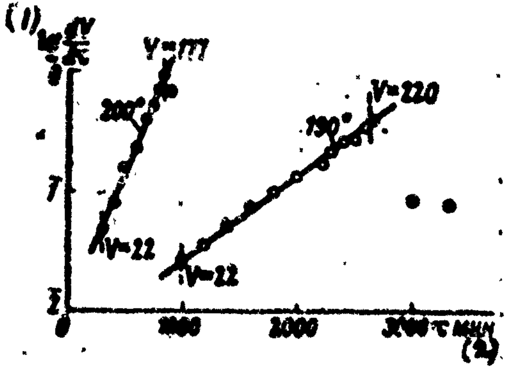

Fig. 14. Check of compliance to the exponential law of the disintegration of styphnate of ammonium at the stage of primary acceleration at various temperatures (m/v ≈ 10^{-3} g/cm^3). (1) log (dV/dτ); (2) τ, min.

Change of disintegration rate in time. Construction of this dependence in logarithmic coordinates, just as for picrate of ammonium, does not give a straight line. Such a line is obtained in the semilogarithmic coordinates log $(dV/d\tau) - \tau$ for temperatures of 190 and 200° (Fig. 14). At 210° and 230° a straight line is obtained at construction in coordinates log $(w - w_0)$ - where w_0 - certain initial values of the disintegration rate, differing for different temperatures.

A significant section of the first stage of the disintegration of styphnate of ammonium is adequately described also by the equation of the autocatalytic reaction

$$\frac{dx}{d\tau} = k_1(a-x) + k_2x^n(a-x),$$

where n lies within the limits 3.5-4 for temperatures of 190-210° and equals 5 at 230°.

Effect of the degree of filling of the vessel (m/v) on the duration of disintegration. As for picrate of ammonium, an increase in m/v (although relatively weakly) the initial rate of gas formation at 210°, but accelerates its growth in time; in exactly the same way, the rate is increased on the second stage (Fig. 15).

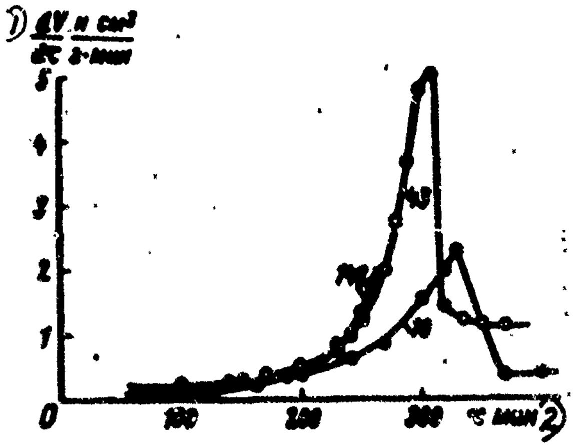

Fig. 15. Influence of m/v on the disintegration rate of styphnate of ammonium at 210°. (Numbers by curves -- m/v in g/cm^3 · 10^4). (1) $(dV/d\tau)$ $\left(\frac{n\ cm^3}{g \cdot min}\right)$; (2) τ, min.

Absolute values characterizing this dependence are given in Table 4.

Table 4

Influence of m/v on the disintegration of styphnate of ammonium at 210°

(1) $m/v \cdot 10^4$ г/см³	(2) $(w_{нач})_1$ в см³/г·мин	(3) $(w_{max})_1$ в см³/г·мин	(4) $(w_{нач})_2$ в см³/г·мин	(5) $\left(\frac{w_{max}}{w_{нач}}\right)_1$	(6) $\frac{(w_{max})_1}{(w_{нач})_2}$
9,8	0,11	2,3	0,35	21	6,6
43,4	0,05	5,0	1,4	100	3,6

(1) g/cm³; (2) $(w_{init})_1$, cm³/g.min; (3) $(w_{max})_1$, n cm³/g.min; (4) $(w_{init})_2$, n cm³/g.min; (5) $(w_{max}/w_{init})_1$; (6) $(w_{max})_1 / (w_{init})_2$

Main dintinctions of regularities of the disintegration of picrate and styphnate of ammonium from regularities of the disintegration of picric and styphnic acids.

The complicated picture of the multistage development of the decomposition reaction of picric acid[1] in the initial stage, including the induction period, then acceleration of gas formation, its fast growth, drop in rate, and subsequent slow acceleration is replaced in the case of picrate and styphnate of ammonium by a two stage course of decomposition. The first stage is strongly accelerated gas formation, proceeding to the achievement of approximately half the final pressure, after which the rate abruptly drops and the second, also self-accelerated, stage of the process begins.

The initial rate in the case of the salts is less than in the disintegration of the acids, but it grows with time significantly, faster, especially at low temperatures. Correspondingly, the pressure of gasiform products of

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[1] Data on the disintegration of picric and styphnic acids --see this collection p 493.

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disintegration of the salts at increased temperatures comparatively early becomes larger than in the disintegration of the acids (Fig. 3). At lower temperatures the disintegration rate salts and acids are levelled later (Fig. 2).

In other words, in the studied interval of temperatures the average rate of disintegration of the salts is somewhat lower than that of the acids at moderate temperatures; at high temperatures it approaches that of the acids.

The disintegration rate of the salts depends more strongly on temperature. This distinction is developed especially clearly if one compares the initial rates, and more weakly with comparison of average rates.

An increase in m/v in the case of the salts somewhat decreases the initial rates of gas formation, but increases analogously that which was observed for picric acid--growth of the rate in time, and also the magnitude and growth of the rate on the second stage.

2. Decomposition of Potassium Salts of Picric and Styphnic Acids

Picrate of Potassium

Picrate of potassium was obtained by pouring a solution of potassium carbonate (7%) into a hot saturated aqueous solution of picric acid (m.p. 122.4°). The small-crystal powder obtained was sifted through a sieve with a mesh dimension of 0.155 mm, and for the experiments we took the part that passed through this sieve. Purity of the picrate was controlled by the determination of the content of potassium (obtained 14.45%, theoretical 14.60%).

The final volume of gasiform products of disintegration constitutes 3.8 moles per mole of picrate of potassium (320 n cm^3/g), i. e., less than for picric acid (410-460 n cm^3/g) and picrate of ammonium (510-530 n cm^3/g). At the end of the experiment a black powder remains on the bottom of the reaction vessel.

The composite results of investigation of the disintegration of picrate of potassium in the temperatures interval 250-300°, in which the picrate is in the solid state, are shown in Fig. 16.

For picrate of potassium the curve of $V = f(\tau)$ or, which is the same, $p = f(\tau)$, has an S-shaped form both for acid and the picrate of ammonium. However, the induction period in case of picrate of potassium is much larger (at 250°, for example, nearly 1000 min), and the subsequent growth of the rat of gas formation and its drop proceed significantly more sharply. This chara of the change in the rate in time at various temperatures is especially clear seen on differential curves (Fig. 17). Curves of $V = f(\tau)$ are well reprodu and are combined (for various temperatures) by a change in the time scale (Fi 18). The disintegration rate of picrate of potassium is a few times less tha that of picric acid or picrate of ammonium (Fig. 19); the difference between them is especially great in the beginning, when decomposition of picrate of potassium is still in the stage of the induction period.

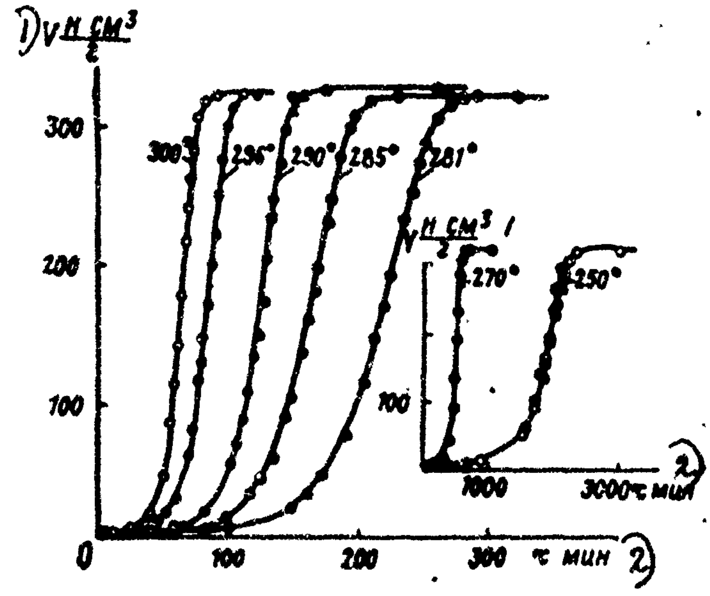

Fig. 16. Disintegration of picrate of potassium at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) $V \frac{\text{n cm}^3}{\text{g}}$; (2) τ, min.

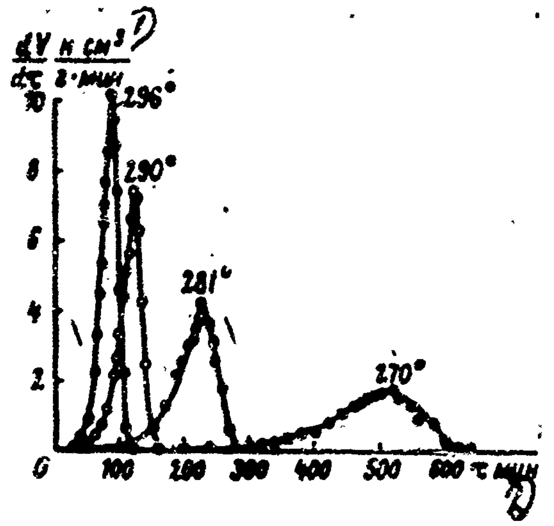

Fig. 17. Changes in the rate of gas formation in time during the disintegration of picrate of potassium at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) ($dV/d\tau$) ($\frac{\text{n cm}^3}{\text{g.min}}$; (2) τ , min.

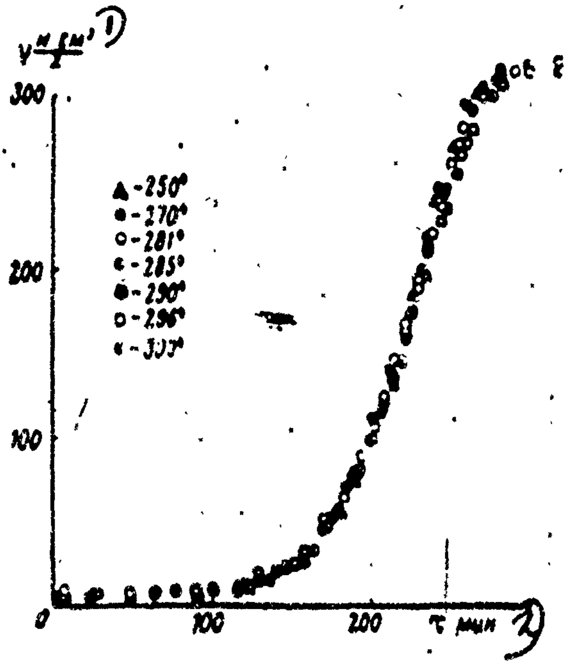

Fig. 18. Combination of curves of $V = f(\tau)$ of the disintegration of picrate of potassium at various temperatures ($m/v \approx 10^{-3}$ g/cm^3).

Values of the coefficient of transformation of the time scale: at 250° - 0.117, 270° - 0.439, 281° - 1.0, 285° - 1.32, 290° - 1.76, 296° - 2.63, 300° - 3.43.

(1) V $\frac{\text{n cm}^3}{\text{g}}$; (2) τ , min.

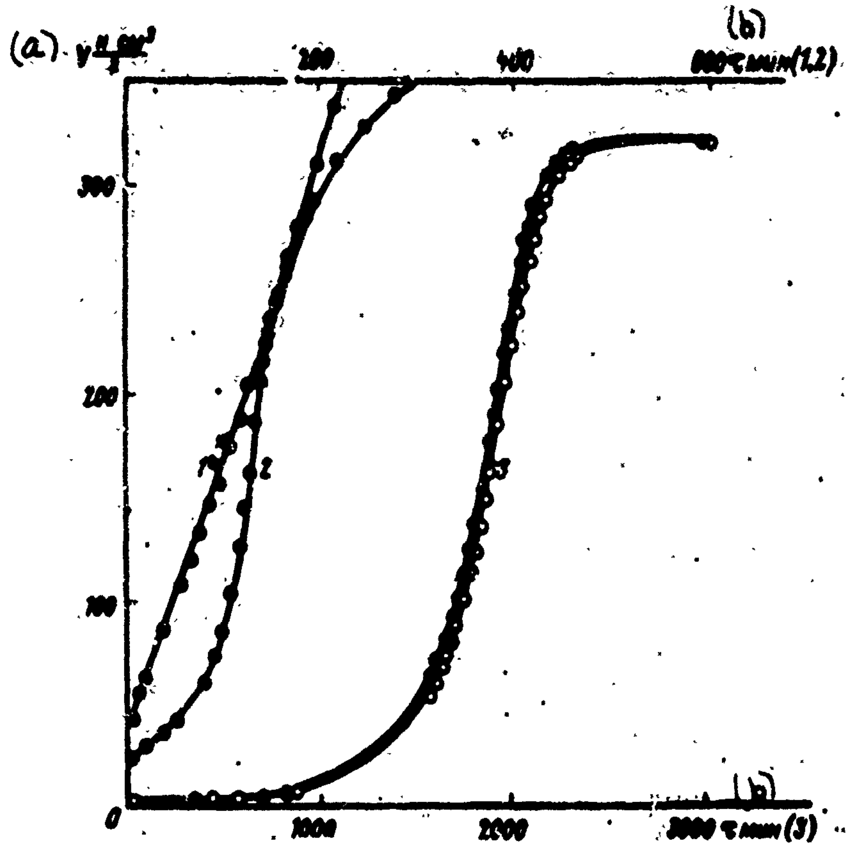

Fig. 19. Comparison of curves of $V = f(\tau)$ during the disintegration of picric acid [1], picrate of ammonium [2] and picrate of potassium [3] at 250° ($m/v \approx 10^{-3}$ g/cm^3). (a) V $\frac{\text{n cm}^3}{\text{g}}$; (b) τ, min.

<u>Dependence of disintegration rate on temperature</u>. By the dependence of coefficient of combination (k_{com}) on temperature in the interval 250-300°, depicted in arrhenius coordinates by a straight line (Fig. 20), E equals 41.2 kcal/mole. The activation energy was calculated also by the temperature dependence of the induction period τ_{ind}, after which was taken the time of emission of 10 n cm^3/g of gases, which corresponded approximately to 3% disintegration (Fig. 20). In this case E = 42 kcal/mole.

<u>Change in disintegration rate in time</u>. This dependence was determined by the construction of curves in coordinates log $(dV/d\tau) - \tau$ and log $(dV/d\tau)$ $-\log \tau$ (Fig. 21). In both cases certain sections of the curve is rectilinear. With this, in logarithmic coordinates this section is larger than in semilogarithmic. However, during an increase in temperature the exponent changes

from 5.5 (at 250°) to 4.5 (at 290°).

We determined also the influence of m/v on the course of the disintegration of picrate of potassium. A change in m/v from $10 \cdot 10^{-4}$ g/cm^3 to $100 \cdot 10^{-4}$ g/cm^3 at 280-300° was not reflected in the induction period, but somewhat accelerated the subsequent development of the reaction. This last influence of m/v is similar to that, which was observed during the decomposition of the majority of the substances studied in this work.

Monopotassium Styphnate

Monopotassium styphnate was obtained by the addition of a calculated quantity of K_2CO_3 to a suspension of styphnic acid (m. p. 178.4°) in boiling water with mixing. The potassium styphnate precipitates out after cooling in the form small yellow crystals. The content of potassium in the product was found to equal 13.7%; by theory in the styphnate monoderivative it equals 13.8%. For the investigation we used crystals which passed through a sieve with a mesh dimension of 0.22 mm and were retained on a sieve with a mesh of 0.19 mm.

According to the general character of the curve of $V = f(\tau)$ (see for example Fig. 22) the disintegration monopotassium styphnate in the studied interval of relatively low temperatures, 170-200°[1], is very similar to the disintegration of the acids, especially picric. The first stage of disintegration of the styphnate is the induction period (Fig. 23), very short at temperatures above 190°, but clearly noticeable at 170°, when its duration constitutes about 20 min. The second stage represents a brief acceleration of gas formation. On the third stage gas formation proceed fast, but with a rate diminishing in time. Maximum pressure, obtainable on the third stage, increases with temperature; at 170° it corresponds to 10 n cm^3/g and at 200° about 75 n cm^3/g. On the fourth

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[1] Above 200° flash occurred.

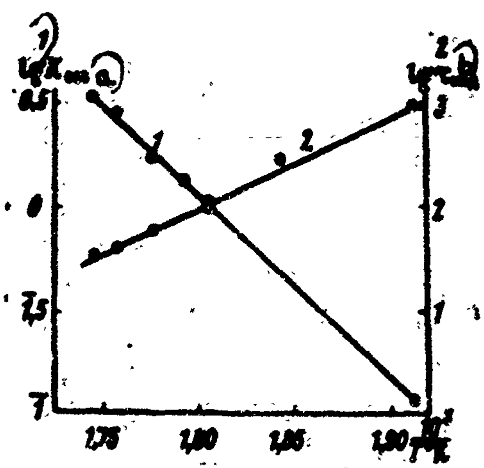

Fig. 20. Temperature dependence of rate of gas formation during the disintegration of picrate of potassium. (1) by the value of the coefficient of transformation; (2) by values of the induction period; (a) log k_{com}; (b) log τ_{ind}.

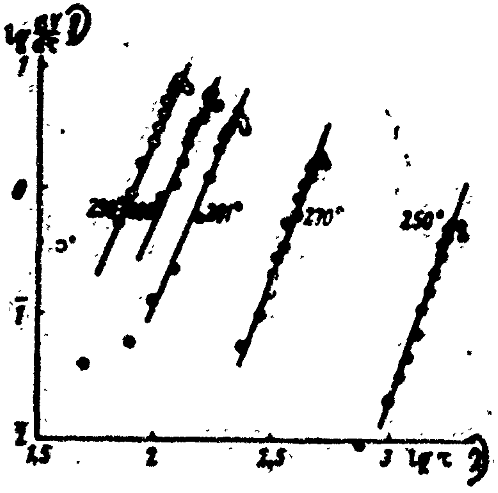

Fig. 21. Dependence of the disintegration rate of picrate of potassium or time. (1) log ($dV/d\tau$); (2) log τ.

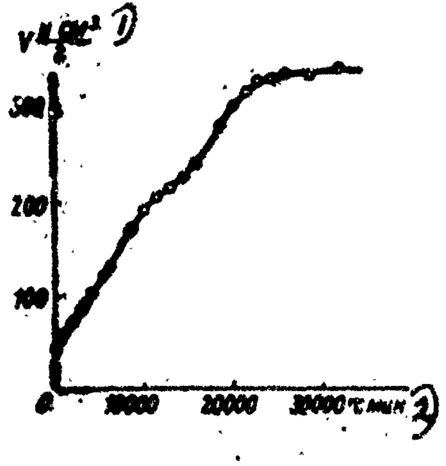

Fig. 22. Disintegration of monopotassium styphnate at 190° ($m/v \approx 10^{-3}$ g/cm^3). (1) $V \frac{n\ cm^3}{g}$; (2) τ, min.

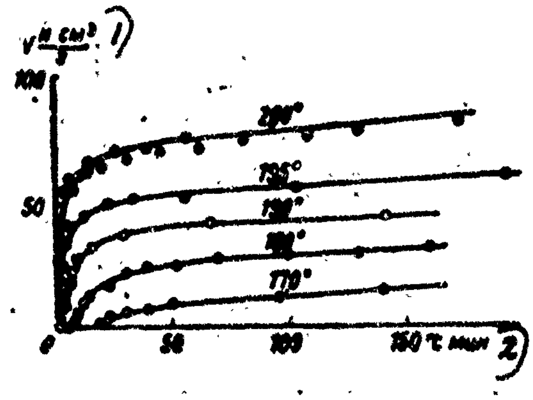

Fig. 23. Initial section of curves of $V = f(\tau)$ during the disintegration of monopotassium styphnate at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) $V \frac{n\ cm^3}{g}$; (2) τ, min.

stage the rate (absolute) is almost constant, but more accurately, grows very weakly in time: thus at 190° the maximum of the rate is in all 20% higher than its value in the beginning of the fourth stage; after achievement of a pressure constituting somewhat more than half the final one, the gas formation rate clearly decreases and the fifth stage is begun, proceeding anew with a certain, more significant growth in the rate (Fig. 24). On the last (sixth) stage, a natural drop in the rate is observed.

All these peculiarities of disintegration are still more clearly visible on differential curves for absolute and, especially, for relative velocity (Fig. 24).

With a similarity of the general character of decay curves of the monoderivative of styphnate and styphnic acid they differ quantitatively very significantly. This distinction, little noticeable in the initial stages, becomes great on the fourth stage, on which for example, at 200° the disintegration rate of the monoderivative of the styphnate is 6 times less than that for styphnic acid (Fig. 25).

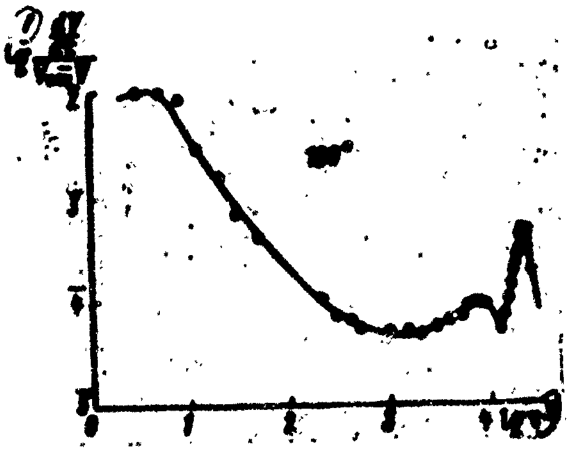

Fig. 24. Change in the relative rate of gas formation in time during the disintegration of monopotassium styphnate (m/v 10^{-3} g/cm^3). (1) $(dV/d\tau) / V_{fin} - V$; (2) log τ.

The temperature dependence of the disintegration rate of the styphnate was determined for the initial rates of the fourth stage by arrhenius lines; the activation energy obtained was equal to 47.6 kcal/mole.

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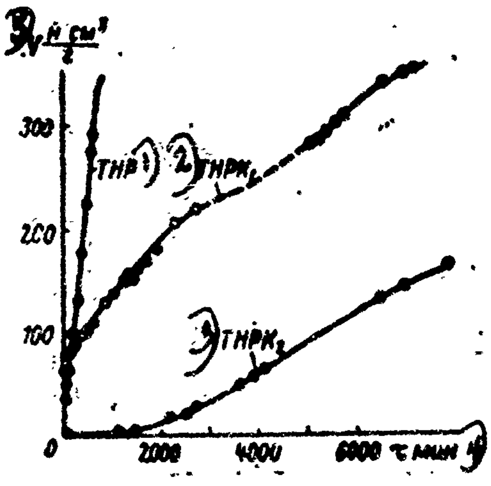

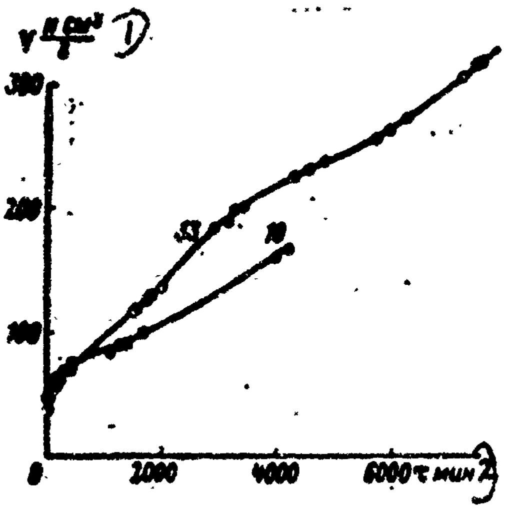

Fig. 25. Comparison of curves of decomposition of styphnic acid (TNR), its derivative ($TNRK_1$), and disubstitution products ($TNRK_2$) of potassium salts at 200° ($m/v \approx 10^{-3}$ g/cm^3). (1) TNR; (2) $TNRK_1$; (3) $TNRK_2$); (4) τ, min; (5) $V \frac{n\ cm^3}{g}$.

Fig. 26. Influence of m/v on the decomposition monopotassium styphnate at 195°. (Numbers by curves - m/v in g/cm$^3 \cdot 10^4$). (1) $V \frac{n\ cm^3}{g}$; (2) τ, min.

A change in m/v weakly affects the initial stages of disintegration, but noticeably increases its speed on the fourth stage (Fig. 26).

Dipotassium Styphnate

Dipotassium styphnate was obtained by the interaction of potassium carbonate with a saturated aqueous solution of styphnic acid, yielding small orange crystals. The obtained product was sifted through a sieve with a mesh dimension of 0.11 mm. The content of potassium in diderivative of the styphnate constituted 24.2% (theoretical content equals 24.3%).

The study of the thermal disintegration dipotassium styphnate was conducted in the interval 200-240°; at 250° under the experimental conditions flash occurred.

In connection with the fact that the styphnate diderivative is crystallized from one molecule of water, for its removal the reaction vessel was pumped for an hour at room temperature and then for an hour at 120°. However, the presence of water vapor is weakly reflected in the course of disintegration, as was shown by comparative experiments on the decomposition of the styphnate diderivative with removal of water and without it.

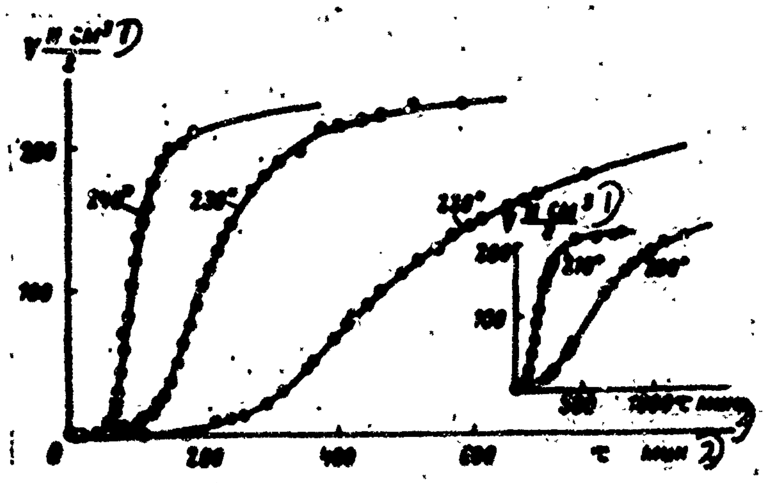

Fig. 27. Disintegration dipotassium styphnate at various temperatures ($m/v \approx 10^{-3}$ g/cm³). (1) $V \frac{n\ cm^3}{g}$; (2) τ, min.

In Fig. 27 are shown the results of experiments at various temperatures, showing the general character of the dependence of $V = f(\tau)$ or, which is the same, $p = f(\tau)$. On the graphics of Fig. 27 and, especially, on differential curves (Fig. 28) it is possible to distinguish three stages: an induction period, a period of acceleration and a period of drop in rate, starting after the achievement of $V \approx 80$ n cm³/g, which corresponds to 35% of V_{fin}. With an increase in the temperature of the experiment there is an increase, as can be seen from Fig. 28, in the maximum of the absolute rate; however, in contrast for example, to styphnate of ammonium there is a growth also in the relative increase of rate (ratio of maximum rate to its initial value). Thus, with a transition from 210 to 230° the ratio w_{max}/w_{init} increases from 2.3 to 5 (Fig. 29).

By the character of disintegration, its acceleration, and the magnitude of the rates dipotassium styphnate is sharply distinguished from the monoderivative, and consequently also from styphnic acid (Fig. 25). At 200° disubstituted styphnate is decomposed 6 times slower than the monoderivative and 23 times slower than the monoderivative and 23 times slower than the acid (comparison was made according to the average rate of gas generation on the section from the beginning of the experiment to the emission of 150 n cm^3/g of gases). At 220° the difference in decomposition rates becomes less.

The dependence of disintegration rate on temperature was determined, first, for the induction period, after which we obtained the time of emission of 10 n cm^3/g of gases. In arrhenius coordinates this dependence is expressed by a straight line and, by the tangent of the angle of inclination of the latter, activation energy equal to 44.8 kcal/mole (Fig. 30, line 1), is obtained.

Secondly, we determined it by the time of achievement of the rate maximum --in other words, by the average rate in the stage of acceleration. This method (Fig. 30, line 2) gives E = 52.9 kcal/mole.

Third, the temperature coefficient of the rate was determined on the section of deceleration of disintegration by the expression for the constants or the reaction rate of the first order (Fig. 30, line 3); in this case the activation energy turned out to be equal to 50.7 kcal/mole.

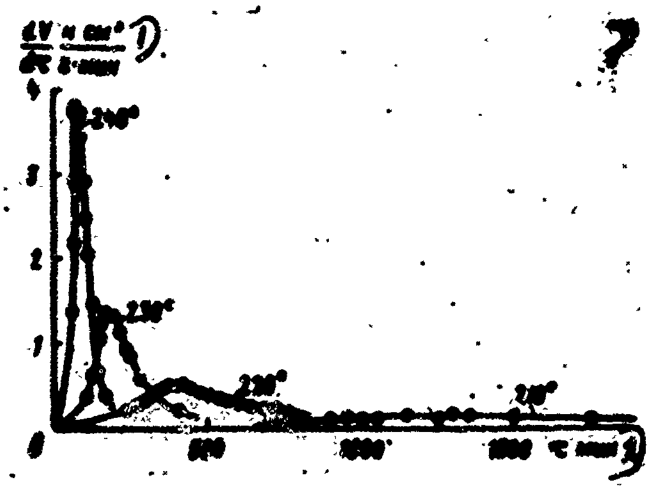

Fig. 28. Change in the rate of gas formation in time during the disintegration of dipotassium styphnate at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) ($dV/d\tau$) ($\frac{n\ cm^3}{g.\ min}$); (2) τ, min.

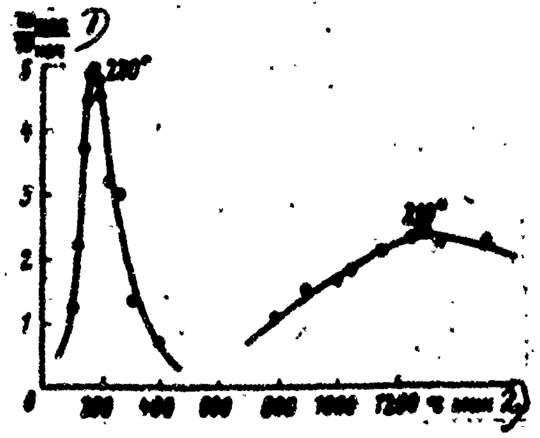

Fig. 29. Change in the relative rate of gas formation in time during the disintegration of dipotassium styphnate at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) w_{max}/w_{init}; (2) τ, min.

Fourth, the temperature dependence was determined by the change in the tangent of the angle of inclination of the rectilinear section of the curve of log V - τ, although, unfortunately, this section was small (degree of disintegration was from 5 to 15% at 200-210° and from 5 to 27% at 220-240°); the given method also gives a straight line in arrhenius coordinates and E = 51.7 kcal/mole.

Change of disintegration rate in time. Attempts to combine the curves of $V = f(\tau)$ for experiments at various temperatures by changing the time scale did not give positive results. Acceleration at high temperatures is greater, than at low ones, in contrast to that which would be expected, for example, during the joint flow of monomolecular and autocatalytic reactions.

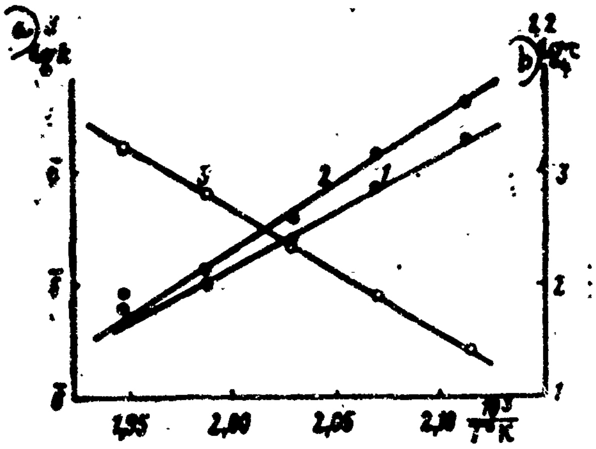

Fig. 30. Temperature dependence of rate of gas formation during the disintegration of dipotassium styphnate ($m/v \approx 10^{-3}$ g/cm^3).

1 - by values of the induction period; 2 - at times achievement of maximum of rate; 3 - by values of the constant of the rate of gas formation in the stage of deceleration of disintegration.

(a) log k; (b) $\log_4 \tau$.

Construction in coordinates ($\log V - \log \tau$) the degree of dependence gives a straight line in a significant interval of decomposition, but the exponent changes, increasing with an increase in temperature from 2.4 at 200° to 5.9 at 240°.

With construction of the curve of $\log V - \tau$ a straight line is obtained only on a small part of its section. Thus the dependence of the rate of gas formation on time is not plotted for dipotassium styphnate in simple relationships of topochemical and chain disintegration.

Influence of the degree of filling of the vessel m/v on the course of disintegration. As was observed also during the disintegration of picrate of potassium, in the case of disubstituted styphnate a change in m/v from 10 · 10^{-4} g/cm^3 to 115 · 10^{-4} g/cm^3 at 230-240° was not reflected in the induction period, but somewhat accelerated the subsequent development of the reaction.

General Regularities Distinguishing the Disintegration of Potassium Salts of Picric and Styphnic Acids

One of the three salts - monopotassium styphnate -- is sharply distinguished with respect to the character of its disintegration from the other two. The disintegration of monopotassium styphnate is qualitatively very similar to that of picric and styphnic acids, but in comparison with the latter it proceeds much more slowly, especially at low temperatures.

The picrate and disubstituted styphnate of potassium are near in type of disintegration: an induction period, acceleration stage, and drop in rate are observed. The styphnate is decomposed significantly (by 40 times) faster than the picrate. Both salts are disintegrated much slower than the corresponding acids. Curves of $V = f(\tau)$ for experiments on the disintegration of picrate of potassium at various temperatures on section of acceleration are combined well with each other by means of a change in the scale of the time axis. In the case of disubstituted styphnate such a combination we are not able to obtain, since at high temperatures acceleration is expressed more strongly than at low ones.

The section of acceleration for the disubstituted styphnate is not plotted completely in the simplest expressions of topochemical and chain reactions; on the section of disintegration rate drop this styphnate obeys the law of reactions of the first order. Known similarity of curves of $V = f(\tau)$ of the average styphnate and picrate is detected with durves of ammonium salts, although without such clearly expressed change as for these last.

3. Decomposition of Lead Salts of Picric and Styphnic Acids

Picrate of Lead

To obtain picrate of lead we added to a saturated solution of picric acid in water, by small portions, crushed lead carbonate lead. The obtained solution was filtered in the hot state and the filtrate was cooled. Picrate of lead precipitated in the form of small yellow crystals, was filtered, washed with benzene, and dried for several hours at 80°.

The content of lead in the obtained product was 30.3%; the theoretical content in the monohydrate of picrate of lead constitutes 30.4%. The picrate of lead was sifted through a sieve with a mesh dimension of 0.15 mm.

After the decomposition of picrate of lead a black powder remained on the bottom of the vessel. A deposit on the walls of the vessel, similar to that which is formed during the disintegration of picric acid and picrate of ammonium, was not observed.

The disintegration of picrate of lead was studied in the temperature interval of 230-260°. At 260° and a sample of 20 mg decomposition in two experiments was completed by flash after 20 min. With a decrease of the sample to 5 mg disintegration passed to completion without flash.

Disintegration starts from a fast growth in pressure (in the process of heating), corresponding to the emission of 35 n cm^3/g of gases at 240-260°. These gases represent, obviously, water[1] bound by the picrate and not escaping during the usual preparation of the experiment (evacuation by a diffusion pump for 2 hr at room temperature).

Curves of $V = f(\tau)$ at low temperatures show a smooth rise without a clearly expressed induction period; the rate of gas formation increases by 9-18 times as compared with its initial value (Fig. 31). The biggest growth (Table 5)

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[1] Emission of 1 mole of water corresponding to 33.0 n cm^3/g of the monohydrate.

is observed at the low temperature of the experiment (230°); with an increase in temperature acceleration decreases, but at 260° again increases somewhat — this, however, can be connected with heating.

After achievement of a pressure constituting about half the final one, the rate passes through a maximum and starts to drop. However, this holds true only near the lower boundary of the studied interval of temperatures (230-240°). At increased temperatures (250 and 260°) the curve already shows a clearly diphasic nature of the process, similar to that observed for styphnate ammonium.

Table 5

Influence of temperature on the course of the disintegration of picrate of lead [m/v = (8.9 to 10.5) · 10^{-4} g/cm^3]

1) t °C	2) $(w_{нач})_1$ в $см^3/г \cdot мин$	3) $(w_{макс})_1$ в $см^3/г \cdot мин$	4) $(w_{нач})_2$ в $см^3/г \cdot мин$	5) $(w_{макс})_2$ в $см^3/г \cdot мин$	6) $\left(\frac{w_{макс}}{w_{нач}}\right)_1$	7) $\frac{(w_{макс})_1}{(w_{нач})_2}$
230	0,023	0,41	—	—	17	—
240	0,094	1,2	—	—	13	—
250	0,23	2,2	2,2	3,1	10	1,0
250	0,28	2,4	2,4	3,0	8,6	1,0
260	0,80	11,0	3,6	7,5	12,5	3,1

(1) t °C; (2) $(w_{init})_1$ n cm^3/g· min; (3) $(w_{max})_1$ n cm^3/g· min. (4) $(w_{init})_2$, n cm^3/g·min. (5) $(w_{max})_2$, n cm^3/g·min; (6) $(w_{max}/w_{init})_1$; (7) $(w_{max})_1/w_{init})_2$

The diphasic nature is especially clearly visible on differential curves (Fig. 32), showing the presence of two maxima of the rate.

Comparison of curves of $V = f(\tau)$ at 230° (Fig. 33) shows that the average rate of disintegration of picrate of lead is significantly less than that of picric acid; however, this distinction is connected mainly with the fact that decomposition of the picrate does not attain the maximum rate at once; this rate is near to the maximum disintegration rate of the acid (Fig. 34).

At 250° and 260° (Fig. 35) the curve of $V = f(\tau)$ for picrate of lead, already starting from half of the disintegration, crosses the curve for the acid. In other words, the disintegration rate of this picrate grows faster with temperature than the disintegration rate of acid; this is analogous to the situation observed for picrate of ammonium.

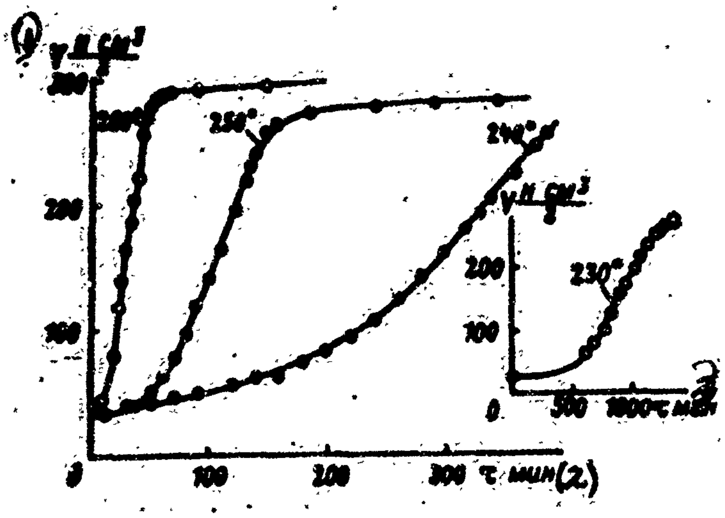

Fig. 31. Disintegration of picrate of lead at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) $V \frac{n\ cm^3}{g}$; (2) τ, min.

Dependence of the disintegration rate of temperature was determined by the coefficients of straight lines in coordinates log $w - \tau$.

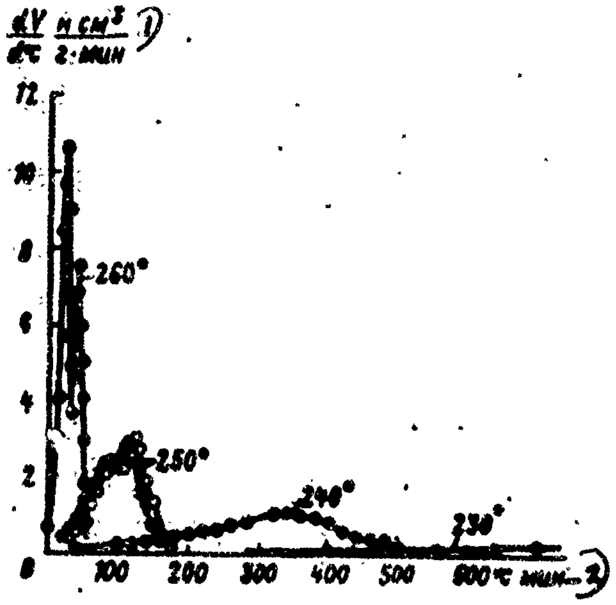

Fig. 32. Influence of temperature on the character of curves of $dV/d\tau = f(\tau)$ during the disintegration of picrate of lead ($m/v \approx 10^{-3}$ g/cm^3). (1) $(dV/d\tau)$ $\left(\frac{n\ cm^3}{g.min}\right)$; (2) τ, min.

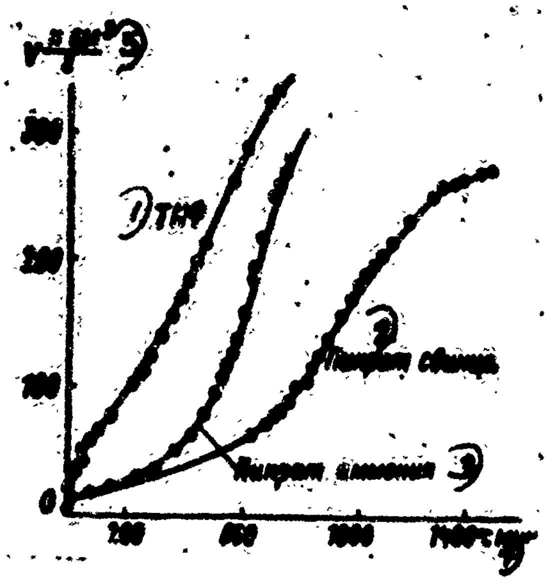

Fig. 33. Comparison of curves of $V = f(\tau)$ during the decomposition of picric acid (TNF), picrate of ammonium, and picrate of lead at 230° ($m/v \approx 10^{-3}$ g/cm^3). (1) TNF; (2) Picrate of lead; (3) Picrate of ammonium; (4) τ, min; (5) $V \frac{n\ cm^3}{g}$.

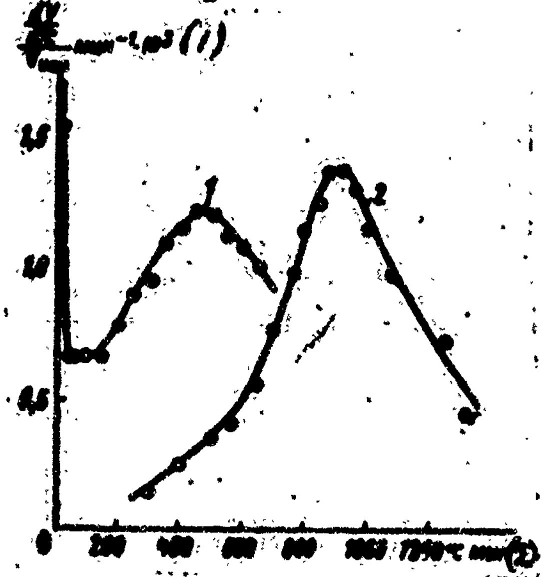

Fig. 34. Comparison of change of rate of gas formation in time during the disintegration of picric acid (1) and picrate of lead (2) at 230° ($m/v \approx 10^{-3}$ g/cm^3). (1) $(dV/d\tau)/V_{fin}$) $min^{-1} \cdot 10^3$; (2) τ, min.

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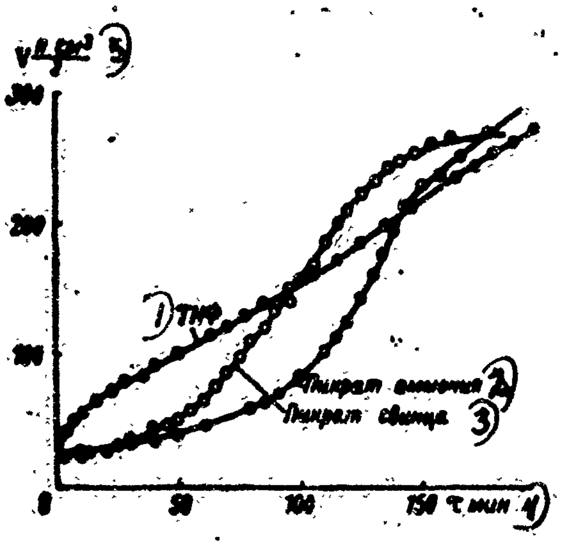


Fig. 35. Comparison of curves of gas formation during the disintegration of picric acid (TNF) and its ammonium and lead salts at 250° ($m/v \approx 10^{-3}$ g/cm^3). (1) TNF; (2) Picrate of ammonium; (3) Picrate of lead; (4) τ, min; (5) V n cm3/g.

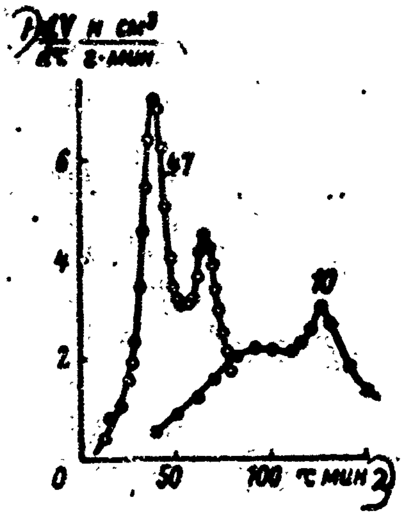


Fig. 36. Influence of m/v on the character of the change in the rate of gas formation in time during the disintegration of picrate of lead at 250°. (Numbers by curves - m/v in g/cm^3 . 10^4). (1) ($dV/d\tau$) (n cm^3/ g. min); (2) τ , min.

The obtained values are plotted on an arrhenius line, by the tangent of whose angle of inclination E = 60.2 kcal/mole. Activation energy was calculated also by the values of the average rates in the interval, where from 30-50 to 140 n cm^3/g of gases will be formed; in this case E = 58.7 kcal/mole. Calculation by the initial disintegration rates gives an acitvation energy of 65.1 kcal/mole. Thus, by all three methods of evaluation, the reaction rate of the disintegration of picrate of lead depends more strongly on temperature than does the disintegration rate of the earlier salts considered.

Change of disintegration rate with time. At 230 to 260° in semilogarithmic coordinates ($\log dV/d\tau - \tau$) a straight line is obtained on a significant section.

With construction of the experimental data in logarithmic coordinates we obtain curves turned by convexity to the axis of the abscissa. If, however, along the axis of the ordinate we plot log ($w - w_0$), then in a certain mean interval of disintegration, corresponding to a degree of transformation of 12 to 43%, we obtain a straight line, but exponent n in the equation $w - w_0 = k\tau^n$ oscillates from 2.0 to 2.5.

<u>Influence of the degree of filling of vessel m/v on the course of disintegration</u>. Determinations were made at a relatively high temperature (250° - see Fig. 36). In distinction from other salts, the course of disintegration picrate of lead is strongly affected by m/v in the entire extent of the process; with an increase in m/v there is an increase in the speed of buildup of pressure on the acceleration section, and a strong increase in the maxima of the rate, especially that first (Table 6). The initial rate increases relatively weakly with an increase in m/v, but acceleration and, correspondingly, the maximum of the rate increase strongly.

Table 6

Influence of m/v on the disintegration of picrate of lead
at 250°

(1) $m/v \cdot 10^4$ г/см³	(2) $(w_{нач})_1$ н см³/г·мин	(3) $(w_{макс})_1$ н см³/г·мин	(4) $(w_{нач})_2$ н см³/г·мин	(5) $(w_{макс})_2$ н см³/г·мин	(6) $\left(\frac{w_{макс}}{w_{нач}}\right)_1$	(7) $\left(\frac{w_{макс}}{w_{нач}}\right)_2$
9,6	0,23	2,2	2,2	3,1	9,6	1,4
47,1	0,30	7,3	3,1	4,5	24	1,5

(1) g/cm³; (2) $(w_{init})_1$, n cm³/g. min; (3) $(w_{max})_1$, n cm³/g.min;
(4) $(w_{init})_2$, n cm³/g. min; (5) $(w_{max})_2$, n cm³/g . min;
(6) $(w_{max}/w_{init})_1$; (7) $(w_{max} / w_{init})_2$.

From Table 6 it is clear that the ratio of the maximum disintegration rate to the initial increases on first stage by $2\frac{1}{2}$ times with an increase in m/v of 5 times; at increased m/v the first maximum is larger than the second.

Styphnate of Lead

Styphnate of lead was obtained by its precipitation from an aqueous solution of styphnate of sodium by an aqueous solution of nitrate of lead. To a saturated solution of styphnic acid (m.t. 178.4°) we added bicarbonate of sodium in small portions. With this there occurs stormy emission of carbon dioxide and the formation of styphnate of sodium. The solution obtained is filtered from mechanical impurities and 0.5 ml. 98-99% acetic acid is added to it. Then the solution is heated to 70-80° and a 7% filtered solution of nitrate of lead is poured into it quickly. With subsequent cooling styphnate of lead is precipitated in the form of small crystals orange in color. The quality of the product was checked by determination of the content of lead, which was found to be 44.2% (the theoretical lead content in the monohydrate styphnate is 44.3%). The styphnate of lead was sifted between sieves with mesh dimensions of 0.19 and 0.16 mm.

In the first experiment water of crystallization was removed by means of evacuation, with heating of the substance to 120-125°, for two hr. With this, on the wall of reactionary vessel there was formed a yellowish deposit. To remove this impurity the styphnate of lead was subjected to preliminary evacuation at 120° for three hr, after which it was poured into another vessel and in the air was again turned into the monohydrate. Further experiments were conducted with just this rehydrated styphnate.

The thermal disintegration of styphnate of lead (Fig. 37) was studied in the temperature interval 200-230°; at 240° (20 mg sample) explosion occurred after 25 sec. No induction period was observed. A fast but small initial increase in its pressure, apparently, connected with the separation of the remainders of water of crystallization. The character of disintegration is clearly two-phase both stages proceed with weak acceleration (Table 7), noticeable even on an integral curve, but clearer on a differential one. The transition from the first to the second stage proceeds after the emission of approximately 40 n cm^3/g of gases, i. e., about ¼ of the total amount of gases emitted during disintegration.

Comparison of the disintegration rates of styphnate of lead, the acid, and other of its salts (Fig. 38) shows that at 200° styphnate of lead decomposes significantly slower (by 3-4 times on the first stage and 8-10 times in the second) than the acid and also then the styphnate of ammonium and monopotassium styphnate, but more quickly than the disubstituted styphnate of potassium.

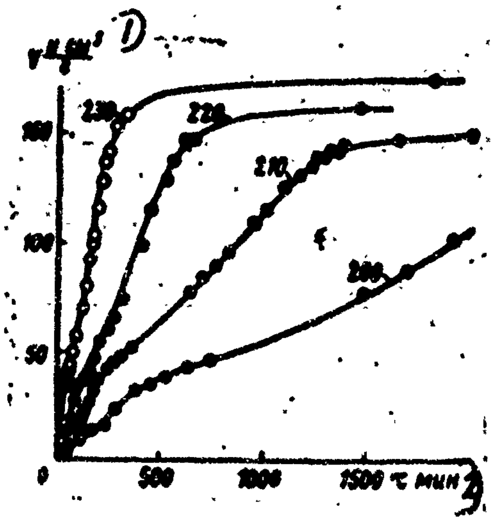


Fig. 37. Disintegration of styphnate of lead at various temperatures ($m/v \approx 10^{-3}$ g/cm^3). (1) $V \frac{n\ cm^3}{g}$; (2) τ, min.

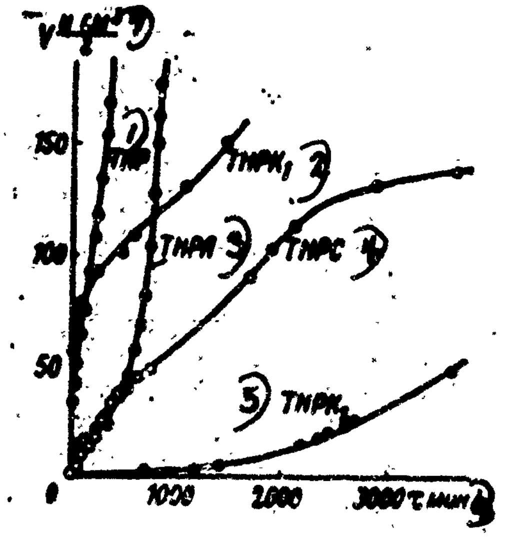


Fig. 38. Comparison of curves of gas generation during the disintegration of styphnic acid (TNR) and its salts; ammonium (TNRA), monosubstituted ($TNRK_1$) and disubstituted ($TNRK_2$) potassium and lead (TNRS) at 200° ($m/v \approx 10^{-3}$ g/cm^3). (1) TNR; (2) $TNRK_1$; (3) TNRA; (4) TNRS; (5) $TNRK_2$; (6) τ, min; (7) $V \frac{n\ cm^3}{g}$.

At 230° (Fig. 39) an analogous picture is observed with the only distinction being that the curve of $V = f(\tau)$ of the disubstituted styphnate of potassium, whose disintegration rate grows faster with temperature, crosses the curve of styphnate of lead.

Table 7

Influence of temperature of the thermal disintegration of styphnate of lead [m/v = (9.8 to 11.9) . 10^{-4} g/cm^3].

(1) t, °C	(2) $(w_{нач})_1$ н см³/г·мин	(3) $(w_{макс})_1$ н см³/г·мин	(4) $(w_{нач})_2$ н см³/г·мин	(5) $(w_{макс})_2$ н см³/г·мин	(6) $\left(\frac{w_{макс}}{w_{нач}}\right)_1$	(7) $\left(\frac{w_{макс}}{w_{нач}}\right)_2$	(8) $\frac{(w_{макс})_1}{(w_{нач})_2}$
200	0,063	0,11	0,034	0,055	1,8	1,6	3,3
210	0,10	0,21	0,078	0,11	2,1	1,5	2,8
220	0,21	0,52	0,16	0,28	2,4	1,8	3,2
230	0,48	1,25	0,31	0,56	2,6	1,8	4,0

(1) t, °C; (2) $(w_{init})_1$, n cm^3/g.min; (3) $(w_{max})_1$, n cm^3/g.min; (4) $(w_{init})_2$, n cm^3/g. in; (5) $(w_{max})_2$, n cm^3/g.min; (6) $(w_{max}/w_{init})_1$; (7) $(w_{max}/w_{init})_2$; (8) $(w_{max})_1/(w_{init})_2$.

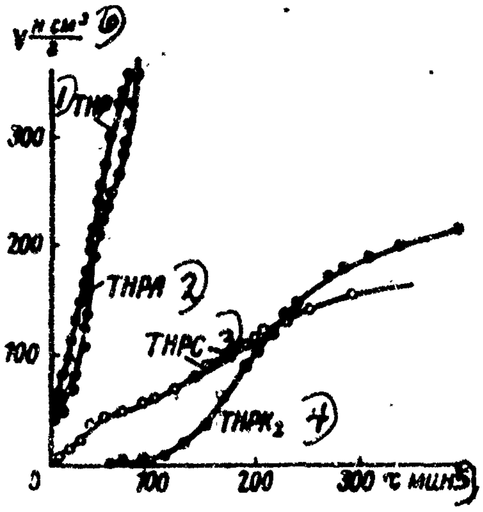


Fig. 39. Comparison of curves of gas generation during the disintegration of styphnic acid (TNR) and its salts; ammonium (TNRA), disubstituted by potassium (TNRK$_2$) and lead (TNRS), at 230° (m/v $\approx 10^{-3}$ g/cm^3). (1) TNR; (2) TNRA; (3) TNRS; (4) TNRK$_2$; (5) τ, min; (6) $V \frac{n\ cm^3}{g}$.

The dependence of disintegration rate on temperature was determined in different ways. By the average rate on the section, where from 10 to 35 n cm^3/g of gases will be separated, i. e. on the first stage of disintegration, we constructed an arrhenius straight line, which gave an activation energy equal to 37.8 kcal/mole.

A near value of activation energy (36.4 kcal/mole) was obtained by construction of an arrhenius line by the values of the constants of the exponential equation for the second stage, and also by the initial rates of the latter (34.8 kcal/mole).

Change of disintegration rate with time. For first stage of disintegration in all studied temperatures intervals the change of gas formation can be expressed by the relationship.

$$\lg(V-V_0)=n\lg\tau+A,$$

where $V_0 = 2$ cm^3/g (Fig. 40). However the values of n is not constant and increases with temperature from 1.14 at 200° to 1.42 at 230°.

For the second stage at all four temperatures (200-230°) we obtain a satisfactory line in the semilogarithmic coordinates $\log V - \tau$ (Fig. 41).

As was already noted, the growth in the rate during the course of disintegration is relatively small in both stages; acceleration is increased with temperature in the first stage from 1.8 (at 200°) to 2.6 times (at 230°); in the second stage the increase in acceleration is still less (1.6-1.8 times).

Influence of degree of filling of vessel on course of disintegration. With an increase in m/v the disintegration rate and its maximum grow (Fig. 42), although not very strongly. Thus an increase in m/v of 10 times (from 12 to 120 . 10^{-4} g/cm^3) led to an increase of the maximum rate of only two times.

General Regularities Distinguishing the Disintegration of Lead Salts of Picric and Styphnic Acids

Characteristic peculiarities of disintegration of both lead salts are their two-stage nature (for styphnate of lead clearly expressed at all temperatures of experiments, for picrate of lead more noticeably at high temperatures) and the absence of induction periods.

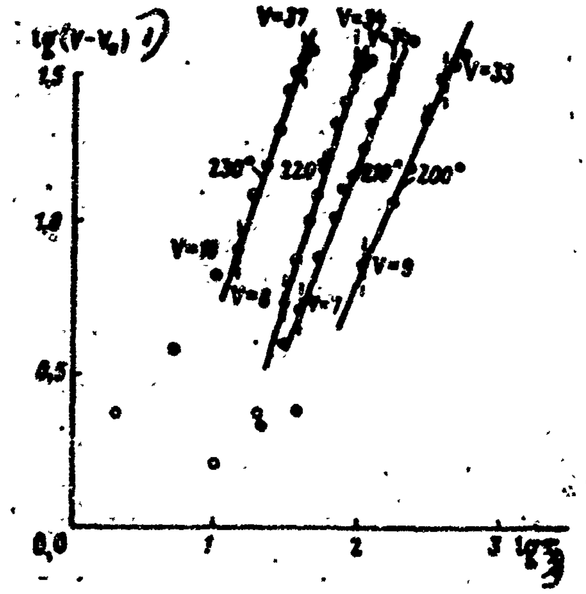


Fig. 40. Rectification of curves of the dependence of quantity of gases formed on time in the first stage of the disintegration of styphnate of lead ($m/v \approx 10^{-3}$ g/cm^3). (1) log $(V - V_0)$; (2) log τ .

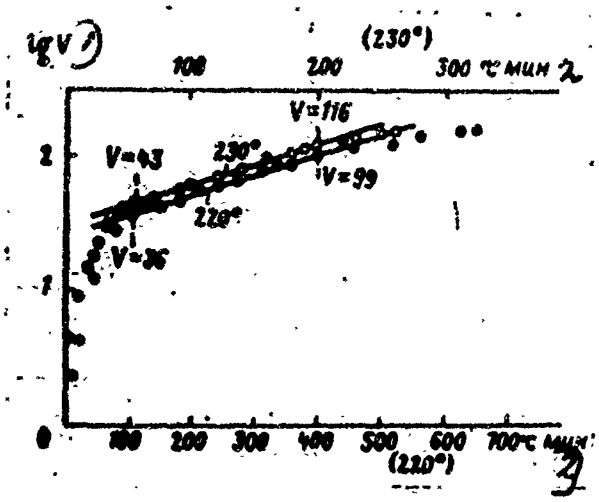


Fig. 41. Rectification of curves of the dependence of the quantity of emitted gases on time in the second stage of the disintegration of styphnate of lead ($m/v \approx 10^{-3}$ g/cm^3). (1) log V; (2) τ , min.

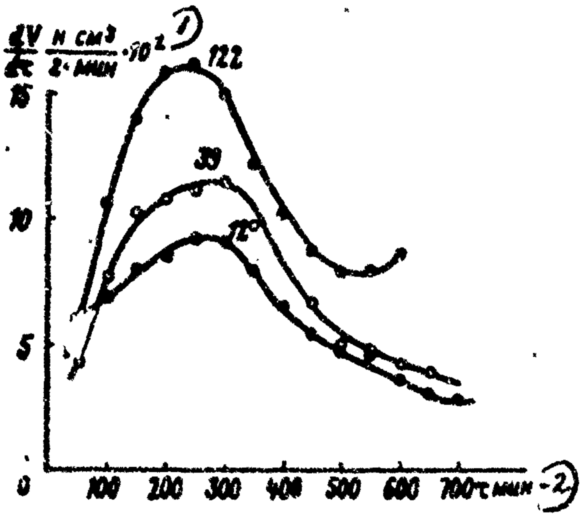


Fig. 42. Influence of m/v on the dependence of the disintegration rate of styphnate of lead on time in the second stage at 200°. (Numbers by curves - m/v in g/cm^3 . 10^4). (1) $(dV/d\tau)$, $\left(\frac{\text{n cm}^3}{\text{g: min}}\right) 10^2$; (2) τ, min.

The main distinctions in the disintegration of the lead salts are the strong dependence of its rate on temperature for picrate of lead ($E \approx 60$ kcal/mole), significantly larger than for acid ($E \approx 37$ kcal/mole); in the case of styphnate of lead, on the contrary, the activation energy is relatively small (~ 35 kcal/mole) and near to that for the acid ($E = 34.6$ kcal/mole). The disintegration rate of picrate of lead grows relatively strongly with time and with an increase in m/v. For the styphnate these dependences are expressed significantly more weaker.

At low temperatures the rate of gas formation during the period of a large part of disintegration of picrate of lead is less than in the case of picric acid; however, the temperature dependence of the disintegration rate of the salt is greater, than that of the acid, as is the acceleration of disintegration in time; therefore with an increase in temperature the picrate is decomposed slower than the acid only in first half of disintegration; in the second half the relationship of the speeds is reversed.

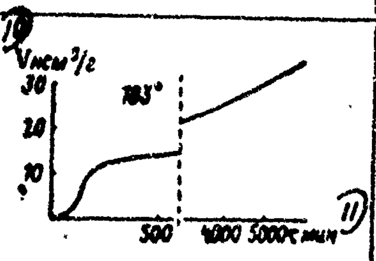
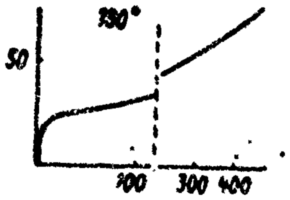
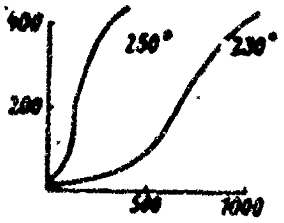
In case of the styphnate the disintegration rate both as low and at increased temperatures remains on its entire extent significantly less than that of the acid.

Discussion of Results

General Regularities of the Thermal Disintegration of Picric and Styphnic Acids and Their Ammonium, Potassium and Lead Salts

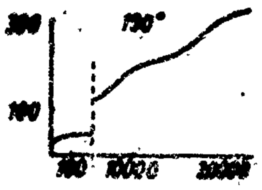
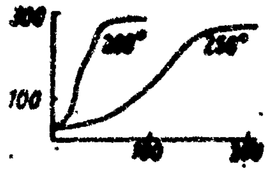
In the decomposition of the enumerated acids and their salts are observed both certain common features and also significant distinctions. For ease of examination the main features of disintegration are represented schematically in Table 8; the values of the activation energy for the substances studied are given in Table 9.

Table 8

1) Вещество	2) Интервал температуры и агрегатное состояние	3) Характер распада	4) Время полураспада при 230° $\tau_{1/2}$ в мин.	K_1^*	K_2^{**}
5) Пикриновая кислота	183—270 8) жидкая		470	1	
6) Стифниновая кислота	180—250 8) жидкая		45	—	1
7) Пикрат аммония	200—270 9) твердый		720	1,53	—

1) Substance; 2) Temperature interval and state of aggregation; 3) Character of disintegration; 4) Time of half disintegration at 230° $\tau_{\frac{1}{2}}$ in min.; 5) Picric acid; 6) Styphnic acid; 7) Picrate of ammonium; 8) Liquid; 9) Solid; 10) Vncm³/g; 11) τ , min.

Continuation Table 8

1) Вещество	2) Интервал температуры и агрегатное состояние	3) Характер распада	4) Время полураспада при 230° $\tau_{1/2}$ в мин.	K_1^*	K_2^{**}
5) Стифнат аммония	190—230 11) твердый		65	—	1,44
6) Пикрат калия	250—300 11) твердый		8600	18,3	—
7) Однозамещенный стифнат калия	170—200 11) твердый		12) 282*** вспышка —200°	—	5,83
8) Двузамещенный стифнат калия	200—240 11) твердый		210 12) вспышка —250°	—	4,67
9) Пикрат свинца	230—260 11) твердый		920 12) вспышка —260°	1,96	—
10) Стифнат свинца	200—230 11) твердый		143 13) взрыв —240°	—	3,18

1) Substance; 2) Interval of temperature and state of aggregation; 3) Character of disintegration; 4) Time of half disintegration at 230°, $\tau\frac{1}{2}$ in min.; 5) Styphate of ammonium; 6) Picrate of potassium; 7) Monopotassium styphnate; 8) Disubstituted styphnate of potassium; 9) Picrate of lead; 10) Styphnate of lead; 11) Solid; 12) Flash; 13) Explosion.

* K_1 - Ratio of periods of half disintegration of picrates and picric acid;
** K_2 - Ratio of periods of half disintegration of styphnates and stypnic acid;
*** - Determined by calculation.

Table 9

Activation Energy E of the Thermal Disintegration of Picric and Styphnic Acids and Their Salts

1) Вещество	2) Интервал температуры °C	3) E ккал/моль	4) Примечание
5) Пикриновая кислота	183—270	38,6	6) E определена по средним значениям скорости при 5—50% распада
7) Пикрат калия	250—300	41,2	8) E определена по совмещению кривых $V=f(\tau)$
9) Пикрат аммония	200—270	43 40,5	10) E определена по средней скорости при распаде от 3—11 до 45% (первое значение) и по тангенсам угла наклона прямых $\lg(V-V_0)=A+k\tau$
11) Пикрат свинца	230—260	60,2 58,7	12) E определена по тангенсам угла наклона прямых $\lg w=A+k\tau$ (первое значение) и по средней скорости при 10—50% распада
13) Стифниновая кислота	180—250	34,6	14) E определена по значениям средних скоростей при 22—45% распада
15) Стифнат калия однозамещенный	170—200	47,6	16) E определена по значениям скорости при 5—35% распада
17) Стифнат калия двузамещенный	200—240	51,7 52,9	18) E определена по тангенсам угла наклона прямых $\lg V=A+k\tau$ при 5—27% распада (первое значение) и по средней скорости на этапе ускорения
19) Стифнат аммония	190—230	45,5 45,5	20) E определена по средней скорости при распаде от 2—9 до 45% (первое значение) и по углу наклона прямых $\lg w=A+k\tau$
21) Стифнат свинца	200—230	34,8 36,4	22) E определена по значениям скорости при ~30% распада (первое значение) и по углу наклона прямых $\lg V=A+k\tau$

1) Substance; 2) Temperature interval, °C; 3) E, Kcal/mole; 4) Notes; 5) Picric acid; 6) E determined by the mean valves of the rate at 5-50% disintegration; 7) Picrate of potassium; 8) E determined by combining of curves of V = f (τ); 9) Picrate of ammonium; 10) E determined by the mean rate during disintegration from 3-11 to 45% (first valve) and by the tangent of the angle of inclination of lines of log $(V-V_0) = A + k\tau$; 11) Picrate of lead; 12) E determined by the tangent of the angle of inclination of lines of log $w = A + k\tau$ (first valve) and by the mean rate during 10-50% disintegration; 13) Styphnic acid; 14) E determined by the valves of the average rate during 22-45% disintegration; 15) Monopotassium styphnate; 16) E determined by the valve of the rate during 5-35% disintegration; 17) Disubstituted styphnate of potassium; 18) E determined by (see following page for continuation of Table 9)

Continuation Table 9

the tangent of the angle of inclination of lines of log $V = A + k\tau$ during 5-27% disintegration (first valve) and by the mead rate on the acceleration stage; 19) Styphnate of ammonium; 20) E determined by the mean rate during disintegration from 2-9 to 45% (first valve) and by the angle of inclination of lines of log $w = A + k\tau$; 21) Styphnate of lead; 22) E determined by the valve of the rate during 30% disintegration (first valve) and by the angle of inclination of lines of log $V = A + k\tau$.

One of the peculiarities of disintegration, inherent in all the compounds studied, is a growth in rate, even the absolute rate, in time on a significant portion of the disintegration. Fall of this rate, caused by a decrease in the concentration (and in the given case, of the quantity) of reagents, which for reactions of the usual type is observed from the very beginning of disintegration, in the case considered set in relatively late.

Those brief sections of drop in rates which were observed for certain of the studied substances are connected not with a decrease in the quantity of reagents, but with a temporary decrease in the role of the factor of acceleration.

Another peculiarity is the deceleration of disintegration during the transition from acid to salt. This circumstance presents definite interest also in the plan of the possibility of using the salts of the acids as thermoresistant substances; if one considers the great induction period of the disintegration of picrate of potassium, the initial speed of its decomposition turns out to be considerably less than for other substances; it is also possible to combine picrate of potassium with oxygen containing salt to increase the ozygen balance and heat of explosion of the misture obtained.

If one were to characterize the deceleration of gas formation by the ratio of the "half-life" of the salts and the corresponding acids, then it constitutes, at 230°, for picrate from 1.5 (for picrate of ammonium) and 2 (for picrate of lead) to 18 (for picrate of potassium). For the styphates the corresponding numbers constitute 1.4 (ammonium), 5 and 6 (di- and monsubstituted potassium salt) and 3 (lead). It is necessary, however, to state that the indicated ration are conditional, since the law of the change in rate is considerably different - in particular, for picrate of potassium the great half-life is in significant measure, determined by the large induction period preceding the growth in the rate speed. Besides, in view of distinctions in the temperature dependence of the rate, the ratio of the "half-life" is different at various temperatures.

From the regularities, common not to all, but only to part of the compounds studied, it is possible to indicate the phasic nature of disintegration.

As a matter of fact, any reaction, proceeding with acceleration can be considered to be phasic, inasmuch as it includes a stage of acceleration and a stage of drop in rate. However, such phasic nature is unavoidable and in this meaning trivial.

The phasic nature of disintegration observed for the studied acids and certain of their salts, has a different and unequal character.

In general the basic type of this phasic nature can be considered a combination of two stages of acceleration, similar to that observed in case of styphnate of ammonium (see Fig. 12), but with large variations both in magnitude of acceleration and in the fraction of gas formation on each of these stages and also in the relative time of their flow. In certain cases at the beginning of decomposition there is observed **an** induction period, were (picrate and disubstituted styphnate of a reverse picture is observed.

The absolute magnitude of the initial disintegration rate of salts, as was already noted is usually less, although in various degrees, than that of the corresponding acids. Since, however, the acceleration for the salts is larger, at a definite stage of disintegration the salt and acid can change places, especially if one were to consider not some one temperature, but the whole interval studied.

The temperature dependence for acids on the main stage of disintegration is samll and is characterized by an activation energy within the limits of 35 - 39 kcal/mole. The comparatively small constant of disintegration rate (for picric acid, for example, at 200° $k = 6.3 \cdot 10^{-7}$ $\sec^{-1}$, if this constant is calculated as for a monomolecular reaction) is caused by the small valves of the pre-exponential multiplier.

For salts the dependence of the rate on temperature is greater. The difference in the activation energies of disintegration of salts and the corresponding acids small for styphnates of ammonium and lead and picrates of ammonium and potassium, but more significant for mono- and disubstituted styphnates of potassium and espicially for picrate of lead.

The increase in the rate in time in many cases and on a more or less significant section can be described by a power or exponential formula. Sometimes, in order to obtain a straight line in these coordinates, one must subtract the initial value of the rate or volume of gasiform products.

An increase in m/v, as a rule, increases[1] the disintegration rate, usually more strongly on the second stage than on the first, obviously as a result of the increase in the pressure of gasiform products of disintegration. This acceleration, however, differs for various substances.

Dependence Between the Kinetic Peculiarities of Disintegration of Picric and Styphnic Acids and Their Salts and the Characteristics of Flash and Burning

One of the promising problems of the investigation was the explanation of

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[1] For picric acid and the picrate and styphnate of ammonium an increas in m/v leads to a certain deceleration of gas formation on its initial stage.

the presence of a possible conformity between the properties of the investigated substances with respect to their flash, inflammability, and burning on the one hand, and slow thermal disintegration on the other.

Consideration of the question, however, is hampered by the circumstance that up till now the flash of picric and styphnic acids, and espically of their salts, has been studied insufficiently; in known measure this applies also to burning -- in this respect there are no systematic data for the picrate and styphnate of ammonium, nor for styphnic acid, itself.

Due to this the comparison of characteristics of different forms of chemical transformation of the studied substances has the character of a preliminary to obtaining fuller data on flash and burning.

Conformity between kinetic characteristics and flash could be expected in two aspects - temperature of flash should be the lower, the bigger is the constant of the disintegration rate[1]; delay time should be larger for substances with strongly expressed induction periods or periods of acceleration of decomposition, and besides for such substances the interval between the temperature at which flash does not occur, and the temperature of flash with a certain small delay should be relatively great.

Further, one could compare kinetic characteristics and intensity of flash, although this last depends in larger measure on regularities of burning (burning rate at increased temperatures and its dependence on pressure) than directly on the kinetics of slow disintegration.

A certain conformity between disintegration rate and minimum temperature of flash is, indeed, outlined. Thus styphnic acid, even with a lesser sample (40 mg,)

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[1] More precisely, the speed of heat emission. It is assumed, however, that the speed of heat emission is emission is proportional to the disintegration rate or speed of gas formation, which directly characterized the disintegration rate in the present investigation.

starts to give flash at a lower temperature than picric acid (100 mg). The minimum temperature of flash of picrate of potassium (20 mg) lies higher than that of styphnate of potassium or picrate of lead.

There are still less data on the inflammability of the studied substances. It is possible only to turn attention to the high inflammability of styphnate of lead, possibly connected with the great speed of its combustion and the correspondingly small thickness of the heated layer. There is a doubt that it is possible to characterize it, in the given case, as for a secondary explosive, by the critical diameter for burning.

The minimum speed, starting from which the burning of many quick-burning explosives is possible, is very great as compared with that observed for secondary explosives. Besides, the experiments of Fogel'zang showed that an increase in the diameter of the charge for the hydrate of picrate of lead from 4 to 7 mm does not lower the critical pressure for burning. Finally, the direct determination of inflammability was hampered by the fact that some of the explosives studied do not burn at atmospheric pressure.

With a comparison of the kinetics and characteristics of burning one could, in the first place, explain whether there is conformity between burning rate and disintegration rate. With an identical type of burning, the bigger the disintegration rate the bigger should be the burning rate. With this one ought to consider also the temperature dependence of the disintegration rate: if for two substances the speed of their decomposition at a certain temperature the courses of a slow process are identical, but depend differently on temperature, than with the stronger dependence the disintegration rate at high temperature, and consequently, the burning rate, should be greater.

Further, it was possible to compare the kinetics and susceptibility of substances to burning, as characterized by the minimum pressure or some other critical parameter of burning. Finally, one could seek a relationship between the kinetics and the dependence of the burning rate on pressure and on initial temperature.

We will start from magnitude of burning rate. It is known that in this respect there exists, at least at low pressures, a sharp distinction between the slowly burning picric acid and its ammonium salt and the fast-burning picrate of potassium and, espeically, picrate of lead. No conformity to this distinction is detected during comparison of the disintegration rates of these compounds. Picrate of potassium is decomposed significantly slower than picric acid, and besides the temperature dependences of their rates are close. Picrate of lead is decomposed slower than picric acid; it is true that the temperature coefficient of its decomposition rate is great and correspondingly one could expect faster disintegration of the picrate at high temperatures. However, as can be seen by the example of the styphnates, this approach is not justified.

One cannot make a comparison with styphnic acid with respect to kinetics and burning rate, since the characteristics of burning of the acid are not determined with sufficient reliability. However, styphnate of ammonium burns very slowly, and styphnate of lead very fast. At the same time both the disintegration rate of styphnate of lead and also its temperature dependence are noticeably less than those for styphnate of ammonium.

The absence of conformity between the disintegration rate and burning rate of the acids and their salts could be connected with differences in volatility, more accurately in relative capability for exothermal reaction in the condensed phase. However, no such distinction is detected during comparison of the nonvolatile salts with each other. Thus styphnate of lead is decomposed slower than both the styphnates of potassium, but burns significantly faster than they do. Picrate of potassium burns (at 20 atm) even somewhat faster than picrate of lead but it is decomposed (at atmospheric pressure) significantly slower.

No conformity is detected between the characteristics of burning of substances and their slow disintegration in the case when the latter is evaluated by the temperature dependence of the rate or by the character of the kinetic curve. Thus, if the disintegration rate of picrate of lead depends significantly more strongly on temperature (in comparison with picric acid), then to say this about the styphnates of lead and ammonium is impossible. If fast-burning picrate of potassium is decomposed with a significant induction period, just as disubstituted styphnate of potassium, then for the still-faster burning styphnate and picrate of lead no induction period is observed. The same can be said in comparing the degree of self-acceleration of disintegration and the influence of m/v on its course.

If as a characteristic of burning we use not the rate, but the ability of substance to burn, then also no clear dependence is detected between this ability and the characteristics of slow disintegration. Of the studied substances (with respect to their ability to burn) styphnate of lead burns easiest of all at the smallest pressure (0.02 atm) and the most difficult of all - picrate of lead (1.8 atm). Picrate of lead is decomposed (at 230°) 6 times slower than the styphnate[1]; this could be connected with its smaller ability to burn. However, disubstituted styphnate of potassium burns with more difficulty (from 3 atm) than monosubstituted, although the disintegration rate of the first is larger than that of the second.

No conformity is revealed between burning rate and ability. At 20 atm it is true, styphnate of lead and monosubstituted styphnate of potassium burn faster than the other; for them the minimum pressure is low. However, picrate of potassium and picrate of lead burn with almost identical speeds but are strongly distinguished in ability to burn. We will add further that the monohydrate of

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[1] It is necessary, however, to mention that the data on burning refer to the monohydrate styphnate of lead, and those on decomposition - to the dehydrate substance.

picrate of lead burns no worse than the dehydrate, and besides its burning rate is even greater.

Till now we have attempted to compare the characteristics of different forms of chemical transformation of the studied substances somewhat formally in order, if successful in detecting such a conformity, to pass to consideration of its physical meaning.

If one were to approach the matter somewhat differently and to imagine what connections it was possible to expect, then besides the natural parallelism between disintegration rate and burning rate one could assume the following regularities:

a) The greater the temperature dependence of the disintegration rate, the easier and faster must the explosive burn, since during burning heating goes undoubtedly to higher temperatures than during the experiments conducted on decomposition. This, however, is not observed (picrate of lead, disubstituted styphnate of potassium; on the contrary, styphnate of lead, with a small temperature dependence of the rate of thermal disintegration, burns easiest of all;

b) If the initial stage of disintegration, leading very probably to dispersion of substance, is only weakly exothermic, then an excessive of speed it, not reinforced by an exothermic processes proceeding near at hand, can hamper propagation of the process; however, if the smaller burning ability of picrate of lead and disubstituted styphnate of potassium could be explained thus, then this explanation is difficult to extend to the remaining studied salts;

c) With a large induction period substance can be heated and, being heated, reacts faster; in this concept a large induction period must relieve propagation of burning; this, however, is not observed, and styphnate of lead, decomposed without a noticeable induction period, burns easier than picrate of potassium, which has the biggest induction period.

In general to find such line of thermal disintegration, which would explain the peculiarity of their burning, is not found for all the studied compounds.

It may be that this is connected with the fact that during burning the speed of heat emission is significant but it should not necessarily be identical to the speed of gas generation, which characterizes thermal disintegration.

It is possible, however, that conformity is absent for a deeper cause, consisting in the fact that the reactions determining propagation of burning are not those or not only those on which the course of slow disintegration depends.

In particular, in reference to burning with dispersion it is possible to suppose that particles will be formed as a result of a little-exothermic reaction and then continue to react in form of burning from the surfact in the gases surrounding them. The main heat input provoking dispersion of a new layer is determined by precisely the reactions of burning of particles; dispersion is not a leading, but a dependant stage of the process and in this meaning relatively little affects the possibility of burning and the speed of its propagation. However, dispersion also can show an influence on the rate of the process: if the particles obtained are large then time of their combustion becomes larger and there is equivalent deceleration of heat emission and consequently of burning.

The conformity between burning rate of suspension and speed of disperision should be known; if the latter is too great, then particles do not burn or burn too far from the surface of the explosive transmit too little heat to it, and therefore burning is not propagated. An increase in pressure, accelerating the burning of particles, strongly increases the speed of displacement of the front of burning and transfers the zone of heat emission more and more into the condensed phase. When this transition is accomplished, a further increase in pressure does not accelerate burning; if, however, the gasiform products are capable of exothermal reactions, then pressure shows the same effect on these reactions and on burning rate which it produces in case of secondary explosives.

Conclusions

1. The kinetics of slow thermal disintegration of ammonium, potassium and lead salts of picric and styphnic acids are studied.

2. The disintegration of all the studied substances has a self-accelerated multistage character, different for various substances, schematically depicted in column 3 of Table 8.

3. The disintegration rate of all salts of a given acid in the studied region of temperatures is on the whole lower than the disintegration rate of the acid itself.

4. Potassium salts are disintegrated slower than lead salts, which in turn are decomposed slower than ammonium salts.

5. The temperature coefficients of disintegration rate for salts are in general greater than those for the corresponding acids; picrate of lead has an especially great temperature coefficient of disintegration rate.

6. The disintegration rates of styphnic acid and its salts are significant larger than those of picric acid and its corresponding salts; the "half-life" at 230° for styphnic acid, styphnate of ammonium, monosubstituted styphnate of potassium, disubstituted styphnate of potassium, and styphnate of lead constitute correspondingly 45, 65, 260, 210 and 143 min.; for picric acid and its ammonium, potassium, and lead salts they are 470, 720, 8600 and 920 min. The strongly increased "half-life" of picrate of potassium is partially connected with the large induction period observed during its decomposition.

7. No clear conformity is detected between the kinetic characteristics of disintegration of the studied explosives and their ability to burn or their rate of burning.

8. Hypotheses are expressed about the mechanism of burning of quick-burning substances, explaining the possibility of absence of a decisive influence of the rate of thermal disintegration on burning rate and burning ability.

Literature

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Tape No. MT-63-254

Pages 401-403 Article No. 25

A. A. Shidlovskiy

25. Thermal Decomposition of Ammonium Nitrate

We know a number of substances which accelerate [3], [4], [5], or delay [1], [2] thermal decomposition of ammonium nitrate. We know also that the speed of thermal decomposition of ammonium nitrate significantly increases after destruction of its crystal lattice (t°_{pl} NH_4NO_3 169°) and, consequently, the most energetic process of decomposition proceeds in a liquid - a fusion of ammonium nitrate.

Earlier, we indicated [4] that the most active catalysts for acceleration of thermal decomposition of a fusion of ammonium nitrate are compounds of hexavalent chrome: chrome trioxide (CrO_3) and bichromates or chromates of potassium or sodium. However, the experiments we conducted showed that at t° = 200° for full decomposition for the duration of 3 - 6 minutes of a small quantity (1 g) of ammonium nitrate a significant catalyst content is required (2 -5% of the weight of decomposable substance).

With a smaller catalyst quantity (1%) intense decomposition of ammonium nitrate did not occur, and losses in weight after the same time with that same temperature did not exceed 2 - 3%.

It was interesting for us to establish how catalysts behave with a significantly increased weighed amount of a fusion of ammonium nitrate, and precisely 10 and 50 g. In all experiments, ammonium nitrate was heated in an air bath to 200 ± 3° (external shell of the air bath was heated in a sand bath).

As a reservoir for the fusion NH_4NO_3 during the experiments with 1 g served a test-tube 15 mm in diameter, with 10 g - a test-tube 35 mm in diameter and with 50 g - a glass 60 mm in diameter.

After bringing the temperature of the fusion NH_4NO_3 to 200° on its surface was poured a weighed amount of powder CrO_3 or $K_2Cr_2O_7$ in a quantity from 0.01 to 0.3 g. After 1 - 2 minutes there occurred dissolution of the catalyst, and then with a sufficient quantity of it, there started vigorous decomposition of the nitrate, accompanied by strong gas formation and significant foaming of the liquid. The temperature of the fusion was then increased (in experiments from 50 g - to 290 - 320°) and in connection with this, the composition of the products of decomposition changed: instead of the colorless nitrous oxide emanating in the beginning, there appeared brown nitrogen peroxide; the whole process of decomposition was finished in 6 - 8 minutes and on the bottom and the walls of the vessel remained only a thin orange-brown deposit of chrome compounds.

With an insufficient catalyst quantity it succeeded in being distributed evenly on the entire mass of the fusion, the fusion was colored an even light-orange, and more phenomena were not observed.

Besides visual monitoring, the loss in weight of ammonium nitrate, occurring after its decomposition was determined. The results of the experiments are in the table.

As can be seen from the table, the quantity of the catalyst, necessary for full decomposition of the fusion NH_4NO_3 , does not grow proportional to the weight of the latter, but significantly slower. Thus for decomposition of 1 g NH_4NO_3 it is necessary to introduce 0.02 g of CrO_3, i.e. 2%, and for decomposition of 50 g, the entire 0.05 g or 0.1% of the weight of the nitrate. In a somewhat less sharp form, the same is observed also for potassium bichromate.

Thermal decomposition of ammonium nitrate with catalytical addition-compounds Cr(VI) - at a temperature of 200 ± 3°.

a) Навеска катализатора г	b) Потеря в весе NH_4NO_3 в % за 6 мин. при весе расплава (в скобках указан % катализатора)		
	c) 1 г	c) 10 г	c) 50 г
CrO_3 0,01	3(1,0)	5(0,1)	—
CrO_3 0,02	100(2,0)	100(0,2)	—
CrO_3 0,03	—	—	3(0,06)
CrO_3 0,05	—	—	100(0,10)
$K_2Cr_2O_7$ 0,01	5(1,0)	—	—
$K_2Cr_2O_7$ 0,02	98(2,0)	2(0,2)	—
$K_2Cr_2O_7$ 0,03	—	95(0,3)	—
$K_2Cr_2O_7$ 0,20	—	—	3(0,4)
$K_2Cr_2O_7$ 0,30	—	—	100(0,6)

a) Weighed amount of catalyst, grams; b) Loss in weight of NH_4NO_3 in % after 6 minutes at the weight of the fusion (in parentheses the % of the catalyst is shown; c) grams.

In experiments with a 50 g fusion, intense decomposition of the nitrate started even up to even distribution of the catalyst on the entire mass of the substance. Consequently, with a large mass of the fusion, the action of the catalyst (% of which is less, but the absolute quantity is more) in a significant measure is local; obviously, the main moment for excitation of violent decomposition of NH_4NO_3 is the creation in the fusion of a zone, in which there would be a sufficiently large concentration of catalyst.

It is possible to assume, although for technical reasons we could not conduct corresponding experiments, that for full decomposition of tens and even hundreds of kg of NH_4NO_3 heated to 200°, it will be sufficient to introduce into it, concentrated in one place, 2 - 3 g of the above mentioned catalysts for triggering in the fusion a focus of intense decomposition, which then will extend on the entire mass of the nitrate. We will indicate also that upon introduction in ammonium nitrate of certain substances (for example $NaNO_3$ or others), lowering its melting temperature, the fusion obtained, probably, can become sensitive to the influence of catalysts of decomposition in a range of lower temperatures, namely 160 - 140°.

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III. BURNING AND FLASH OF EXPLOSIVES

K. K. Andreyev

26. Concerning the Question of the Factors Determining the Dependence of the Burning Rate of Explosives on the Initial Temperature And Pressure

General considerations

It is known that for solid fuel, applied in a semiclosed volume, the smallest dependence of burning rate on initial temperature and pressure is desirable. If burning rate grows proportionally with pressure or faster, then such fuel cannot be used in the noted conditions. The value of the dependence of burning rate on pressure and on temperature is seen graphically from the equation of balance of intake of gas during burning and its discharge

$$u_m S = A\sigma p, \qquad (1)$$

where u_m — mass burning rate;

S — surface of burning charge;

σ — plane of critical section of nozzle;

A -- coefficient of expenditure;

p — pressure in chamber.

If we express, as is frequently done, the dependence of burning rate on initial temperature and pressure by the empirical relationship

$$u_m = \frac{Bp^{\nu}}{A_1 - B_1 T_0}, \qquad (2)$$

where B, A_1 and B_1 are constants, then putting (2) in (1), we obtain

$$\frac{B \cdot p^{\nu} S}{A_1 - B_1 T_0} = A\sigma p. \qquad (2a)$$

Determining from (2a) equilibrium pressure, we have

$$p=\left[\frac{BS}{A\varkappa(A_1-B_1T_0)}\right]^{\frac{1}{1-v}}. \qquad (3)$$

From equation (3) it is clear that the dependence of equilibrium pressure on charge and chamber parameters/ is determined by the dependence of burning rate on pressure (through quantity v).

The dependence of equilibrium pressure on initial temperature is stipulated not only by the dependence of burning rate on temperature, but also simultaneously by its dependence on pressure. Indeed, from (3)

$$\frac{dp}{dT_0}\cdot\frac{1}{p}=\frac{1}{1-v}\cdot\frac{B_1}{A_1-B_1T_0}. \qquad (4)$$

In other words, the relative change of equilibrium pressure during a change of initial temperature of the fuel is determined both by its influence on burning rate (through the second multiplier), and also by the dependence of burning rate on pressure (through the first multiplier).

We will imagine two fuels whose burning rate depends equally on temperature, increasing twice with its increase by 100°, if their v one different, pressure during burning in a semiclosed volume with this change of temperature will grow by a various number of times. If, for example, $v_1 = 0.5$, and $v_2 = 0.75$, then pressure will be increased by 4 and 16 times respectively. Therefore the search for a fuel with a small dependence of burning rate on temperature is of practical interest only in that case when this will not lead to an increased dependence of burning rate on pressure. In supplement to the above one should make precise that meaning which is contained in the concept "dependence of burning rate on pressure". If we consider this dependence, as was done above, in the usual form

$$u_n=\beta p^v, \qquad (5)$$

then of the two magnitudes, determining magnitude of velocity at a given pressure, only one is essential for equilibrium during burning in a semiclosed volume. In reality the baric coefficient of burning rate

$$\frac{du_{\text{н}}}{dp}\cdot\frac{1}{u_{\text{н}}}=\frac{\beta\nu p^{\nu-1}}{\beta p^{\nu}}=\nu\frac{1}{p} \qquad (6)$$

at a given pressure depends only on magnitude v, and not on β .

We will define now the temperature coefficient of burning rate. This can be done in two ways. If we take, according to Belyayev and Zeldovich [1], that exothermal reactions will go only or chiefly in the gaseous phase and that burning rate correspondingly is determined by a reaction proceeding at a temperature practically equal to the temperature of burning, then the dependence of rate on the temperature of burning, and through it on the initial temperature, can be expressed by the relationship

$$u_{\text{н}}=\gamma T_b^{k} e^{-E/2RT}, \qquad (7)$$

where T_b —temperature of burning, connected with the initial temperature T_o by the relationship

$$T_b=T_0+\frac{Q}{c_p}, \qquad (8)$$

in which Q is the thermal effect of burning, cp is the average heat capacity of products of burning from T_o to T_b, and k is a constant whose value depends on the order of the reaction and for a monomolecular reaction equals 3/2.

From (7) we have

$$\frac{du_{\text{н}}}{dT_b}\,\frac{1}{u_{\text{н}}}=\frac{1}{T_b}\left(k+\frac{1}{2R}\,\frac{E}{T_b}\right). \qquad (9)$$

From (9) is clear that temperature coefficient of burning rate should decrease with growth of initial temperature, although insignificantly [1]. With this it is the less, the higher is the temperature of burning and the less the activation

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[1] Change of initial temperature cannot be large as compared to temperature of burning.

energy of the leading reaction. This means that for substances with a high burning rate the coefficient shown should be less than for substances with a low rate, since a high rate of burning signifies high temperature of the course of the leading reaction or a low energy of its activation, or both together.

An alternate method of appraisal of dependence of burning rate on temperature is based on this, also following Zeldovich [5], that one takes the burning rate to be determined by speed of propagation of the thermal wave created by the reaction in the condensed phase; then its dependence on temperature will be expressed by the relationship

$$u = \frac{1}{\rho' c'_p (T_k - T_0)} \cdot \sqrt{2\eta' Q' A' e^{-E'/RT_k} \frac{RT_k^2}{E'}}, \qquad (10)$$

where u — burning rate, equal speed of thermal wave;

ρ' — density condensed phase;

c'_p — its heat capacity;

T_k — maximum temperature, to which there can be a condensed phase; in case of volatile substances — boiling point;

η' — coefficient of thermal capacity of condensed phase;

Q' — thermal effect of reaction;

A' — pre-exponential factor in the expression for reaction rate in the condensed phase;

E' — activation energy of reaction in condensed phase.

Designating

$$\frac{1}{\rho' c'_p} \sqrt{2\eta' Q' A' e^{-E'/RT_k} \frac{RT_k^2}{E'}} \quad \text{through} \quad \varphi,$$

we will obtain the dependence of burning rate on initial temperature in the form

$$u = \frac{\varphi}{T_k - T_0}. \qquad (10a)$$

This expression is similar with that, which flows from the hypothesis of Mikhelson and Mallyar—Le Chattelle [7]; they, as it is known, considered propagation of burning to be a result of heatup by gaseous products of burning of unreacted substance to a certain critical temperature, analogous to the temperature of flash. Well-grounded and constructive criticism of this hypothesis as the universal mechanism of burning is given in the works of Ya. B. Zeldovich and D. A. Frank-Kamenetskiy [4].

Reality of first or second mechanism of Zeldovich in the concrete case is determined by the properties of the substance and the conditions under which burning occurs. If the substance is low-volatile, then this favors flow of reaction in the condensed phase. Reaction rate in the gaseous phase depends on the pressure, under which burning occurs, since it is proportional to pressure in the first (monomolecular reactions) or higher degree. By this cause it is possible to imagine such a case, when at low pressures processes in the condensed phase have the predominant significance, but at higher ones — in the gaseous phase.

Apparently the burning of unitary fuel on the based on nitrocellulose and liquid nitro esters represents just such a case. At very low pressures the burning rate does not depend on pressure [6]. This shows that the gaseous phase reaction is not leading in these conditions.

In the area of moderate pressures (atmospheres) the burning rate depends so strongly on temperature that calculation by formula (7) leads to unreally high values of activation energy. Side by side with this the temperature coefficient of burning rate increases with an increase of initial temperature, which is in contradiction with dependence (7) and agrees with expression (10a). Finally, the temperature coefficient of speed depends on pressure, decreasing an increase in the latter, which is again impossible to coordinate with dependence(7). All this forces us to assume that at low pressures, especially if the initial temperature of the fuel is high, the burning rate is determined by reaction in condensed phase, but at high pressures —basically in the gaseous phase.

In the intermediate region propagation of burning is determined by the totality of the processes occurring in both phases: the lower the pressure, the greater the role played by transformation in the condensed phase, and vice-versa. For those conditions, relationship (10a) is correct, the temperature coefficient of burning rate is determined by the expression

$$\frac{du}{dT_0} \cdot \frac{1}{u} = \frac{1}{T_u - T_0}. \qquad (11)$$

Analysis of Experimental Data

We will try to compare experimental data with the general considerations considered in the preceding section.

In connection with by the fact that the existing theory of Zeldovich and Belyayev considers burning of individual chemical compounds, we will take as a basis for comparison data obtained for a series of explosives belonging to lose classes of chemical substances (nitro esters and nitro compounds), to which the main components of contemporary unitary fuels belong. Further, at atmospheric and moderately increased pressures the process of burning ordinarily can be complicated by secondary, unconsidered influences (outward thermal losses, variable incompleteness of reaction, remoteness of zone of maximum temperature from burning surface, etc). Therefore the main determinations for the establishment of dependence of burning rate on pressure were conducted at pressures higher than 50 and, in many cases up to 1000 atm.

The main problem in the comparison of experimental results with conclusions of theory was checking the accuracy of the latter. If one can confirm this accuracy, even in certain simplest conditions —for example, at high pressures and for individual compounds— then the very same theory would receive more durable support, than it has today, and this would allow to make the following step to the description of the burning of multicomponent systems and to the calculation of those disturbances that are stipulated by lowering of pressure.

Results of investigation of the dependence of burning rate on pressure for a series of studied substances one given in Table 1 and are graphically presented in Fig. 1.

Table 1

Dependence of burning rate of certain explosives on pressure

1 Взрывчатое вещество	2 Интервал давления *ат*	3 Значения коэффициентов в формуле $u_м = A + Bp^{\nu}$ *			4 Скорость горения $u_м$ при 100 *ат* *г/см²сек*
		A	*B*	ν	
5 Тротил	20—950	0,04	0,00716	1	0,76
6 Пикриновая кислота	25—950	0,14	0,00805	1	0,95
7 Тетрил	10—250	0,0	0,0630	0,695	1,55
8 Гексоген	100—1000	0,90	0,0216	1	3,06
9 Дина	20—100	0,12	0,00912	1	1,02
10 Тэн	15—750	0,0	0,0193	1	1,93
11 Нитрогликоль желатинированный (97:3)	1—150	0,075	0,0315	1	3,22
12 Нитроглицерин желатинированный (95:5)	10—320	0,8	0,0592	1	6,72

* u_m expressed in $g/cm^2 sec$, and p in kg/cm^2.

1) Explosive; 2) Pressure range atm; 3) Value of coefficients in the formula $u_m = A + Bp^{\nu}$ *; 4) Burning rate u_m at 100 atm, g/cm^2sec; 5) Trotyl; 6) Picric acid; 7) Tetryl; 8) Hexogen; 9) Dyne; 10) PETN; 11) Nitroglycol, gelatinous (97:3); 12) Nitroglycerin, gelatinous (95:5).

We see that for almost all substances dependence of burning rate on pressure in the studied interval of the latter is near to linear; with this, in many cases especially for volatile and slowly decomposed substances, member A in the expression $u_m = A + B_p{}^{\nu}$ is near to zero, but ν is near to 1, so that the dependence shown is turned into a direct ratio. From the point of view of the theory, such a result means that a bimolecular reaction is leading during burning. The same shows that at least in the studied interval of pressures the majority of these explosive are themselves little useful for stable burning in a semiclosed volume.

At a pressure of 100 atm the burning rate of the substances shown in Table 1 differ at most by 9 times. The trotyl has the lowest speed (0.76 g/cm^2 sec), and gelatinous nitroglycerine, characterized by a high heat of burning, the highest (6.7 g/cm^2 sec).

In connection with this there appears the question, of whether one can consider as the main parameter, determining the magnitude of an explosives burning rate the heat (or temperature) of its burning. It is known that in powder practice such a connection for ballistite powder is taken both by us and abroad.

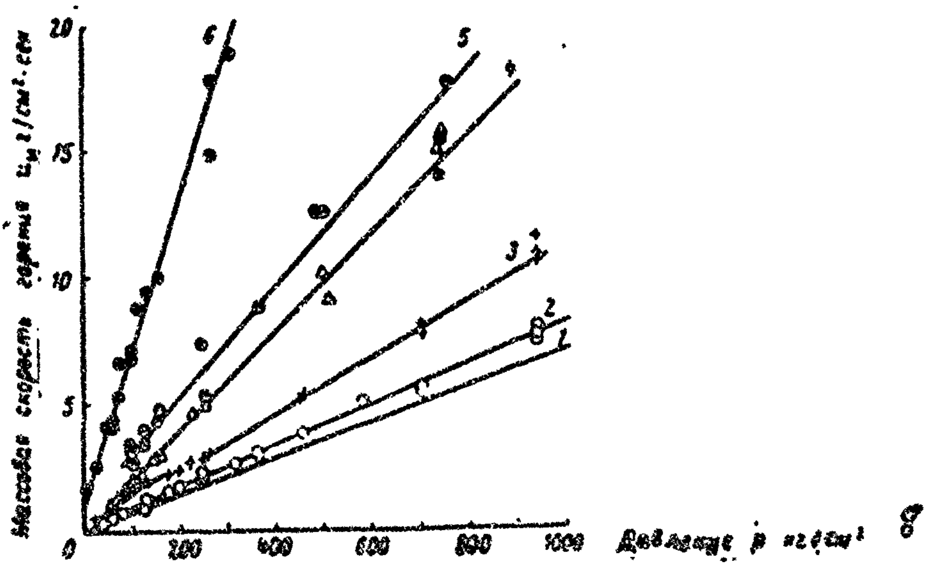


Fig. 1. Dependence of burning rate of certain explosives on pressure.

1—trotyl, 2—picric acid, 3—tetryl, 4—PETN, 5—hexogen, 6—gelatinous nitroglycerin; 7—Mass burning rate u_mg/cm^2 sec; 8—Pressure p, kg/cm^2.

We usually express it by the formula of the Special Technical Bureau (OTB) [2]

$$u_1 = (0{,}16Q_L - 32) \cdot 10^{-4},$$

where u_1 →calculated burning rate at 1 atm in g/cm^{2}sec, but

Q_L —heat of burning with liquid water in kilocalories for 1 kg powder.

If the calculated speed is referred to a pressure equal to 100 kg/cm^2, then the formula takes the form

$$u_{100} = (0{,}16Q_L - 32) \cdot 10^{-2}.$$

Muraour [9], on the basis of his own numerous investigations, which led him to the formula expressing dependence of burning rate on pressure

$$u = a/2 + b/2p,$$

established that coefficient b (burning rate is expressed in mm/sec) is connected with temperature of burning by relationship

$$\lg(1000b) = 1{,}214 + 0{,}308T_b/1000$$

or

$$\lg b/2 = -2{,}087 + 0{,}308T_b/1000.$$

Thus in both cases it is assumed that burning rate depends only on the heat emanating during burning, or on the temperature at which it is obtainable, but not on the kinetics of the chemical transformation.

This assumption can be interpreted differently. Thus it can be said that intermediate reactions differ, but the leading reactions are one and the same—for example, the interaction between oxide of nitrogen and oxide of carbon.

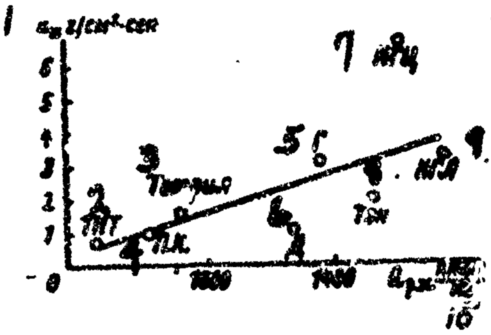


Fig. 2. Dependence of burning rate of certain explosives on its calculated heat.
1)Um, g/cm^{2}sec; 2)TNT; 3)Tetryl; 4)Picric acid; 5)Hexogen; 6)Dyna; 7)Nitroglycerin; 8)PETN; 9)Nitroglycol; 10)Q p.l. (KCal/kg).

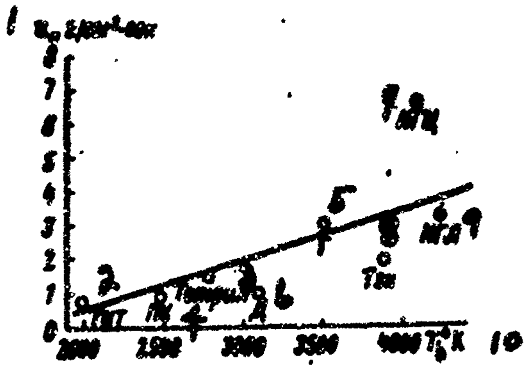


Fig. 3. Dependence of burning rate of certain explosives on its calculated temperature.
1-9) Same as Fig. 2; 10) T_b, °K.

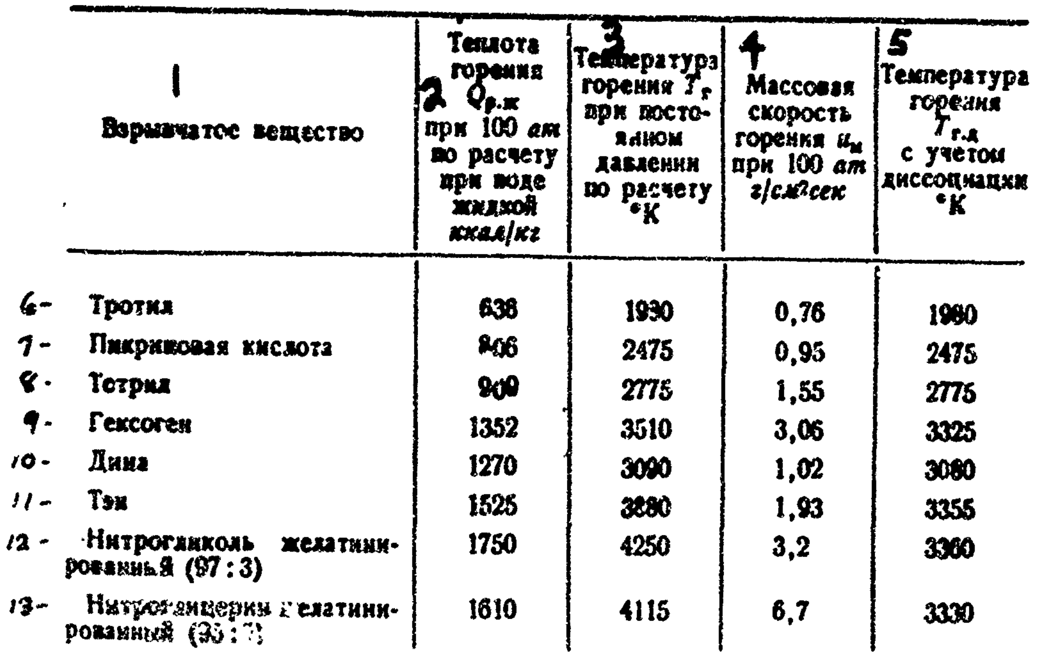
In such a case speed of propagation of transformation indeed would depend only on the temperature which will be attained during it. It would have been possible to allow also that the transformation of any one of the main components is leading, while diluents play other roles and are reflected in the speed of the process only in that measure, in which their presence changes the temperature of burning. It was excluded finally that the formulas of the OTB and Muraour have an approximate character and reflect only that fact that the speed of reactions during burning increases with temperature. By a comparison of heat, temperatures, and burning rates of explosives, referring to different classes of chemical formations, it was possible to explain which of the given assumptions is correct. In Table 2 and on the graph of Fig. 2 the values of heat and speeds/ burning of at 100 atm are given for certain explosives.

We see that for five substances —nitroglycol hexogen, tetryl, picric acid, and trotyl —the relationship between burning rate and heat is near linear and can be expressed by the relationship $u_{100} = (0.235Q - 124) \cdot 10^{-2}$. The points for PETN and dyna lie significantly below the line. In Fig.3 and 4 are shown the dependences $u_m = f(T_b)$ and $\log u_m = f(T_b)$. The first of them is naturally analogous to the dependence of u_m on Q p. 1. Points expressing the second dependence can be placed on two parallel lines: 1:$\log u_{100} = -1.115 + 0.470T_b/1000$ and 2:$\log u_{100} = -1.495 + 0.470T_b/1000$.

Thus from comparison of experimental data with both forms of the empirical dependence of burning rate on its thermal effect, it follows that these dependences are not universal, have an approximate character, and reflect only the fact that the burning rate, generally speaking, grows with an increase in burning temperature.

Table 2

Heat, temperature, and burning rate of certain explosives



	1 Взрывчатое вещество	2 Теплота горения $Q_{р.ж}$ при 100 *ат* по расчету при воде жидкой *ккал/кг*	3 Температура горения $T_г$ при постоянном давлении по расчету °K	4 Массовая скорость горения $u_м$ при 100 *ат* *г/см²сек*	5 Температура горения $T_{г.д}$ с учетом диссоциации °K
6-	Тротил	638	1930	0,76	1980
7-	Пикриновая кислота	806	2475	0,95	2475
8-	Тетрил	909	2775	1,55	2775
9-	Гексоген	1352	3510	3,06	3325
10-	Дина	1270	3090	1,02	3080
11-	Тэн	1525	3880	1,93	3355
12-	Нитрогликоль желатинированный (97:3)	1750	4250	3,2	3360
13-	Нитроглицерин желатинированный (95:5)	1610	4115	6,7	3330

1) Explosive; 2) Heat of burning Q p.l. at 100 atm by calculation/during water of liquid kcal/kg; 3) Temperature of burning T_b at constant pressure by calculation, °K; 4) Mass burning rate u_m at 100 atm, g/cm^2.sec; 5) Temperature of burning T_{bd}, taking into account dissociation, °K; 6) Trotyl; 7) Picric acid; 8) Tetryl; 9) Hexogen; 10) Dyna; 11) PETN; 12) Nitroglycol, gelatinous (97:3); 13) Nitroglycerin, gelatinous (95:5).

Dependence of burning rate on temperature is described by the theory of burning of Belyayev and Zeldovich. It was of interest to clarify whether this dependence is in better agreement with the facts. Graph of Fig.5 gives in coordinates $\log\frac{u_n^2}{T_b^2}-\frac{1}{T_b}$.

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We see that general character of this dependence is analogous to the one considered earlier. The substances studied can be placed on two lines, and besides for nitro esters the tangent of the angle of inclination of the lines is greater than that for nitro compounds. Consequently, and this comparison confirms conclusions made above about the approximate character of connection between heat and burning rate even for explosives homotypic in character of burning and also illustrates the similarity of all considered dependences.

Thus, not only the temperature of burning, but also kinetics of chemical transformation is an essential factor, determining the magnitude of the burning rate. This conclusion becomes even more convincing, if the temperature of burning is calculated for a series of substances with dissociation taken into account. In internal ballistics of artillery barrels this is usually not done, since we have the matter of large pressures, where dissociation can be disregarded. For conditions of the ballistics of a semiclosed volume, in particular, for those pressures to which are connected the results we considered, calculation of dissociation leads to an essential change of temperature of burning; this change is the greater, the higher the temperature of burning and the greater the oxygen balance of the explosive.

In Table 2 one given the values of the temperature of burning for eight explosives without calculation and taking into account of dissociation. We see that in the last case the temperatures for hexogen, PETN, nitroglycol and nitroglycerin are very close and are within the limits 3340 ± 20°K, then that the burning rates of certain of them differ by 2—3 times.

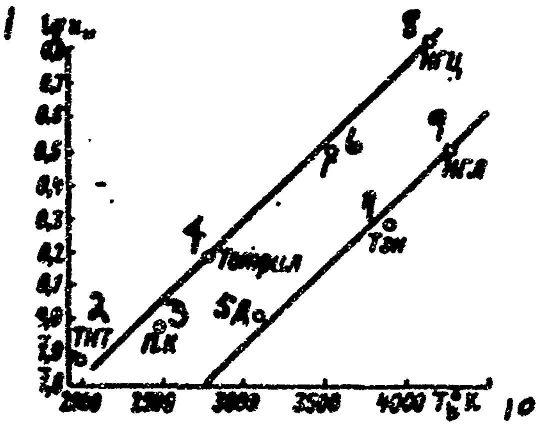

Fig. 4. Dependence of burning rate certain explosives from its calculating temperature in coordinates log u_m —T_b.

1) Log v_m; 2) TNT, 3)Picric acid; 4) Tetryl; 5) Dyna; 6) Hexogen; 7) PETN; 8) Nitroglycerin; 9) Nitroglycol; 10) T_b, °K.

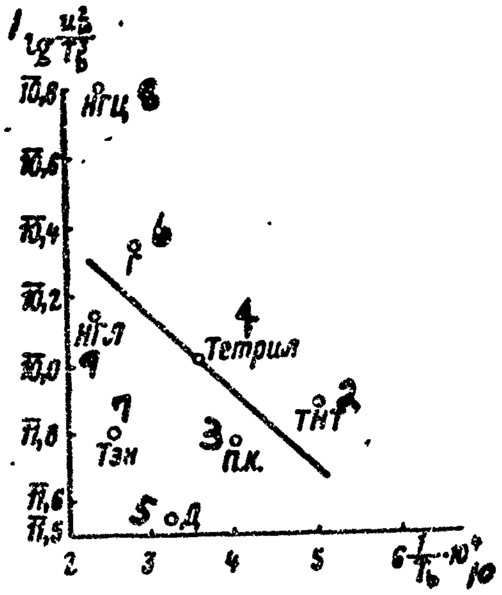

Fig. 5 Dependence of burning rate certain explosives from its calculating temperature in coordinates log (u^2/T_b^3) - $1/T_b$.

1) Log Um^2/T_b^3; 2-9) Same as Fig. 4; 10) $(1/T_b).10^4$.

The conclusion that the burning rate of a volatile explosive depends not only on the temperature of burning does not contradict the Belyayev — Zeldovich theory which considers the activation energy of chemical transformation during burning to be a second essential factor on the given dependence. However, if the difference in speed of this process for explosives close in terms of temperature of burning is determined by the differences in activation energy, then this should be reflected in the difference in dependence of burning rate on temperature. In order to check this conclusion, we conducted experiments on the determination of dependence of burning rate of two explosives (tetryl and PETN) on the temperature of burning. A change of the latter can be realized in two ways —by a change of the initial temperature of the explosive ($T_b = T_o + \frac{0}{cp}$) or by diluting it with an inert impurity. The last method allows a change of temperature of burning in wider limits, but the selection of an impurity which would be indeed inert is difficult and can be confirmed only by comparison of data obtained in both ways. In frames of this work was realized only the second method with the application for the thermal dilution of the explosive of water, which is one of the products of burning and is a sufficiently chemically inert substance.[1]

Results of experiments are given in Table 3, and results of calculation conducted on the basis of these data are presented in Fig. 6.

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[1] These experiments were conducted by student V. A. Poyasov (tetryl) and Engineer P. P. Popova (PETN).

Table 3

Influence of water on burning rate of tetryl and PETN at a pressure of 100 atm

1 Содержание воды в % по весу	2 u_m г/см²сек	3 T_b °K по расчету	4 Примечание
	5 Тетрил (по Поясову)		
0	1,55	2795	6 Плотность образчиков была в пределах 1,21—1,35 г/см³
0	1,56		
2,38	1,32	2675	
2,68	1,35	2640	
4,38	1,20	2535	
5,98	1,12	2485	
	7 Тэн (по Поповой)		
0	1,93	3880	8 Плотность образчиков заключалась в пределах 1,2—1,3 г/см³
1,63	1,75	3775	
2,43	1,60	3735	
3,62	1,39	3645	
5,40	1,18	3535	

1) Contents of water in wt%; 2) um, g/cm^2.sec; 3) T_b, °K by calculation; 4) Notes; 5) Tetryl (per Poyasov); 6) Density of samples was within the limits 1.21—1.35 g/cm^3; 7) PETN (per Popova); 8) Density of samples fell within the limits 1.2 — 1.3 g/cm^3.

We see that, in the first place, the change of the burning rate from its calculated temperature in coordinates $\log u^2/T_b^3$ — $1/T_b$ is depicted by a straight line. Thus this requirement of theory is fulfilled. Secondly, it is possible to calculate the energy of activation for the given process by the slope of this line. For tetryl it constitutes about 7 kcal/mol, if the reaction is considered bimolecular and its speed is taken as proportional to the square of concentration. For PETN the value, obtained analogously is about 47 kcal/mol. We saw higher that if we judge by the temperature scale, PETN belongs to the class of slow-burning substances. Results of the determination of the dependence of burning rate on burning temperature are in agreement with this conclusion. Other conditions being equal, high energy of activation signifies a lower burning rate. We will add also that the relatively low burning rate of PETN (and dyna) shows that burning rate does not change parallel with the speed of slow thermal disintegration, since PETN as well as dyna, is decomposed significantly faster than nitro compounds or nitramines of the aromatic series, with this nitro esters have higher calculated temperatures of burning.

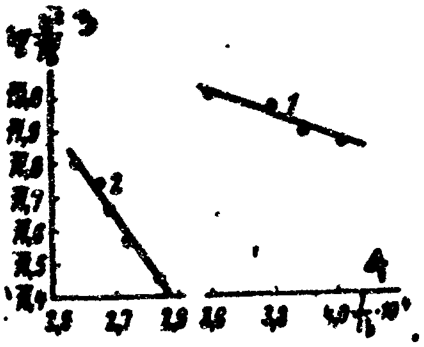

Fig. 6. Dependence of burning rate of tetryl and PETN on their calculated temperatures, regulated by the contents of water.

1) Tetryl; 2) PETN; 3) Log U^2/T_b^3; 4) $(1/T_b) . 10^4$.

On the Theoretical Connection Between Temperature (Heat of Burning) And Dependence of Burning Rate on Initial Temperature And on Pressure

In connection with the fact that in the frames of investigations conducted, although they were limited, the observed regularities of burning do not contradict theoretical, we have a basis to consider another interesting technology of the dependence, issuing from the existing theory. From these positions let us consider the question of the temperature coefficient of the burning rate and its dependence on the heat of burning. It is usually considered that high-calorie solid unitary fuels display a larger dependence of burning rate on temperature, than fuels of lesser caloricity. This conclusion is made on the basis of practical experience obtained with fuels whose caloricity is changed by changing of the contents of nitroglycerin. Above, we saw that temperature coefficient is connected with the temperature by dependence (9)

$$\frac{du_{n}}{dT_{b}}\cdot\frac{1}{u_{n}}=\frac{1}{T_{b}}\left(k+\frac{1}{2R}\cdot\frac{E}{T_{b}}\right),$$

from which it follows that it is the lower, the higher is the temperature of burning.

In the light of these data it is natural to assume that an increase in the temperature dependence of burning rate of fuels based on nitroglycerin with an increase in the contents of the latter is stipulated not by the increase in the caloricity of the mixture, but by the kinetic peculiarities (high energy of activation E) nitroglycerin. If this single contradiction with theory can be thus removed, then we assume, as a conclusion from the theory, the position that "hot" fuels should develop smaller dependences of burning rate on initial temperature than "cool" ones. An experimental check of this conclusion presents indubitable interest. If it is confirmed, it will be possible to concentrate on the search for substances which combine high heat of burning with small activation energy. We will add that such substances simultaneously would be relatively quick-burning, since according to the theory the combination of high burning temperature and small activation energy should(other conditions being equal)lead to a high burning rate.

We will touch now on the question of the dependence of burning rate on pressure. The theory connects it with the order "n" of the leading reaction, establishing the proportionality of burning rate to pressure in the degree n/2. The proportionality of burning rate to the first degree of pressure, determined by experiments at elevated pressures, can be interpreted as the result of the bimolecularity of the leading reaction. However the same experiments show that at pressures lower than 100 atm, the burning rate depends on pressure sometimes more and sometimes less. The first may be connected with a change in the completeness of the reaction at low pressures near that at which burning becomes possible; the second —near the beginning of the linear section of the change of burning rate —with the possibility of partial flow of reaction in the condensed phase.

When an exothermal reaction in a significant interval of pressure occurs in a noticeable degree in the condensed phase as, for example, occurs during the burning of nitrocellulose, the burning rate grows with pressure more slowly than according to the law of direct proportionality.

Finally, reaction of first order may present itself as leading as, judging by data of English investigations [8], occurs during the burning of hydrazine. A radical means of lowering the dependence of burning rate on pressure is the use of substances like picrate of potassium, whose burning rate is independent of pressure, apparently because the leading reaction in this case occurs in the condensed phase. With known prerequisites with such character of burning the dependence of burning rate on initial temperature is small.

The experiments whose results were used in the present article were conducted by A. P. Glazkova, I. A. Tereshkin [3], and P. P. Popova, and the largest part of the calculations by I. A. Tereshkin. The author expresses his gratitude to them.

Conclusions

1. The dependence of burning rate on pressure for a series of secondary explosives belonging to the class of nitro esters and nitro compounds is near to direct proportionality. It follows from this, according to the Zeldovich — Belyayev theory, that the leading reaction during the burning of substances of this class is bimolecular.

2. Burning rate of a series of explosives can be approximately connected with the heat and temperature of burning by a linear dependence. A similar dependence is obtained in the coordinated $\log U^2/T_b^3 - 1/T_b$.

3. Quantitative analysis of the latter dependence shows that it, as well as the first two dependences, has an empirical and approximate character.

4. It was shown by the method of dilution by inert impurity of two substances (PETN and tetryl) that the dependence of their burning rates on its calculated temperature are identical in character and are in agreement with the theoretical, but differ quantitatively: stronger for PETN than for tetryl.

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Chapter 3 Article 27

Pages 416-429

K. K. Andreyev

27. The Burning of Nitrates of Certain Alcohols

Combustion of explosives is usually caused by their ignition. It can appear also during local decomposition, if the latter leads to a warm-up sufficiently strong that it terminates in local self-ignition. The character of the emerging combustion and its degree of stability depend on the properties of the substance and conditions of burning.

For nitrates of alcohols the typical peculiarities of the burning process were determined basically during investigation of nitroglycol (NGL) and nitroglycerine (NG). The results of this investigation and their explanation are considered in the present article.

Limiting Conditions of Normal (Undisturbed) Burning

Experiments set up by the usual method (burning of a liquid poured into a narrow glass test-tube in an instrument of constant pressure with windows, photographic registration of the character and speed of propagation of the process), showed that burning is possible only if the diameter of the charge, the pressure and the temperature are not too small [3]. The effect of these parameters is determined by the fact that at too low a pressure and temperature the speed of chemical reactions and, consequently, also heat liberation are insufficient to compensate with a small diameter for heat loss of combustion products and the heated layer of substance to the outside. Increasing the speed of reactions by means of increasing pressure or temperature, and also decreasing relative heat loss by means of increasing diameter and increasing initial temperature of the substance remove the predominance of heat loss over heat gain and burning becomes possible. Thus, limiting ourselves to pressure, NGL in test-tubes with a diameter of 4 mm at room temperature burns, starting from a pressure of 300 mm Hg, and NG, under analogous conditions, at a pressure of 24 mm and higher.

Transition of Normal Burning of Nitroglycol to a Turbulent Regime

With an increase of pressure the burning rate of NGL grows approximately proportional to the pressure, similarly to that observed for many solid substances, for example, for trinitrotoluene, trinitrophenol, etc. However while for trinitrotoluene and picric acid this dependence is observed throughout the large range of pressure studied (to 1000 atm), for NGL the burning rate grows proportionally to the pressure only approximately up to 20 atm [4]. With this pressure the character of burning changes; the surface of the liquid ceases to be even and horizontal and periodically is distorted; the process takes on a pulsating character and becomes a sequence of alternated flashes, divided by periods of delayed burning.

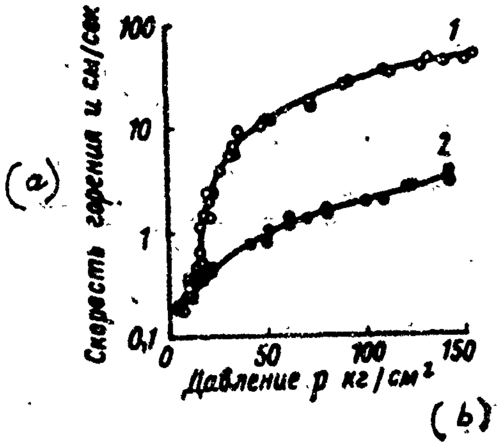

Fig. 1. Dependence of burning rate of nitroglycol on pressure.

1--liquid, 2--nitroglycol, gelatinized by collodion (97:3).
a) Burning rate u cm/sec; b) Pressure p, kg/cm^2.

Transition into a pulsating regime is accompanied by a strong (approximately ten times) increase of average speed of burning; in transitional region values of speed vary greatly. At further increase of pressure speed grows linearly and much faster than in the normal regime (Fig. 1), and irregularity of burning is not detected.

One should point out one more peculiarity of burning which develops with an increase of pressure. At low pressures, burning takes place with a slight glow

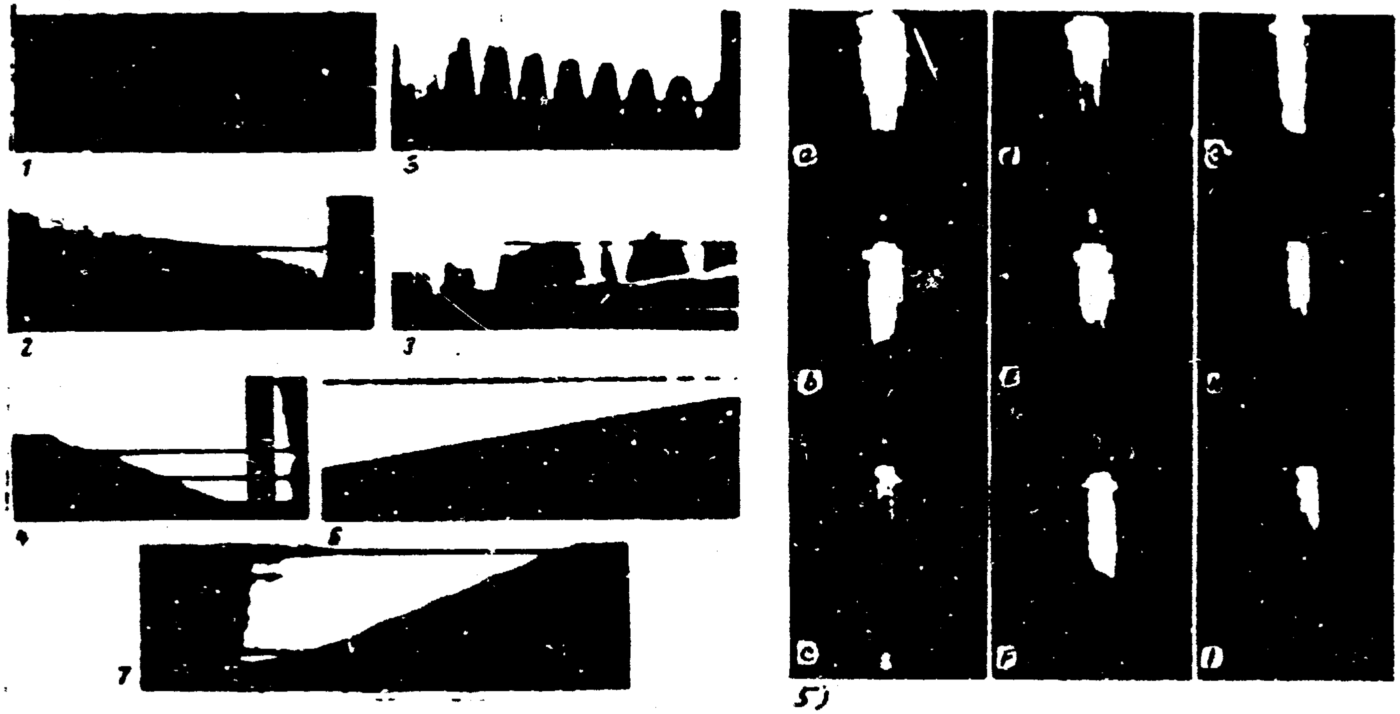

Fig. 2. Burning of nitroglycol and supercooled liquid dyna (Photographed with the help of photoresister and high-speed movie camera)

1) at 6 atm—undisturbed burning of NGL without secondary flame, 2) at 15 atm—undisturbed burning of NGL with primary and secondary flames, 3) at 15 and 17 atm—pulsating burning of NGL with periodic approach of secondary flame to surface of liquid, 4) at 53 atm—interval between flames of burning NGL indiscernible, 5) at 16.5 atm—consecutive photographs of burning NGL, made with high-speed movie camera; noticeable approach and rejection of secondary flame from surface of liquid, 6) at 52 atm—burning of dyna undisturbed, 7) at 5[illegible] atm—burning of dyna is pulsating.

adjacent to the surface of the liquid, and during this the flame has the usual form —a cone, pointed upward . At a pressure of about 10 atm (the magnitude of this pressure decreases with an increase in tube diameter) at a significant (about 2 cm) distance from surface of liquid there appears a bright bluish flame in the form of a cone, pointed downward . The appearance of the secondary flame is accompanied by a sharp change of composition of gases —nitric oxide is completely reduced to nitrogen. This will lead to a strong (approximately double) increase in heat and, correspondingly, temperature of burning. The appearance of secondary flame is not reflected, however, either in the speed or in the character of burning. With further increase of pressure the distance between primary and secondary flame is decreased and at 60 and more atmospheres becomes indiscernible.

The peculiarities described are illustrated by the photographs in Fig. 2. An especially clear pulsation is noticeable on them thanks to the presence of a bright secondary flame (Fig. 2, photo 3a). When distortion of the surface occurs, the heated layer of substance is cooled and evaporation is delayed. As a result of this the secondary flame approaches the surface of the liquid, and then is rejected from it, when violent decomposition occurs in the heated layer formed, which is thicker than normal.

An increase of initial temperature, increasing the speed of normal burning, decreases the pressure at which the turbulent regime appears and strengthens the dependence of the burning rate on pressure in this regime (Fig. 3).

Methylnitrate and diethyleneglycoldinitrate will behave similarly to NGL. For the first of them, burning with relatively great speed (0.14 g/cm^2 sec at 1 atm) transition to the turbulent regime occurs at a pressure of about 2 atm; for slowly burning diglycoldinitrate this is observed approximately at 55 atm. With this same pressure the burning of liquid dyna supercooled to room temperature also changes into a pulsating regime. The burning rate of dyna is also relatively small.

Fig. 3. Dependence of burning rate of nitroglycol on pressure at various temperatures.

Disturbance of Normal Regime of Burning of Nitroglycerine

During the burning of NG phenomena are observed, similar to those described above, but with certain quantitative and qualitative differences [2]. At a pressure higher than 24 mm Hg the burning rate of NG, while significantly exceeding the burning rate of NGL, slowly grows with pressure; at a pressure of about 1 atm during igniting something like a local flash is observed, accompanied by a splash of liquid, and burning in this case does not appear. Moreover, if NG is ignited in a tube with a diameter of about 4 mm at low pressure and burning takes place in closed volume so that pressure grows, then after attaining about 300 mm Hg burning spontaneously dies out. Pressure of attenuation strongly depends, as was shown in experiments of G. N. Bespalov [1], on diameter of tube. With a diameter of 2.6 mm burning dies out at 150 mm Hg. With a tube diameter of 10 mm burning occurs up to a pressure of 1050 mm Hg. Thus it is possible to observe the burning of NG also at atmospheric

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[1] See present collection (page 432 of original text).

pressure. However this was attained only with one of the various studied methods of igniting —igniting at lowered pressure with a subsequent slow increase of pressure to atmospheric. Application of other methods caused turbulization and, as a result, attenuation of burning. Burning rate of NG at atmospheric pressure constitutes 0.146 cm/sec or 0.23 g/cm^2 sec.

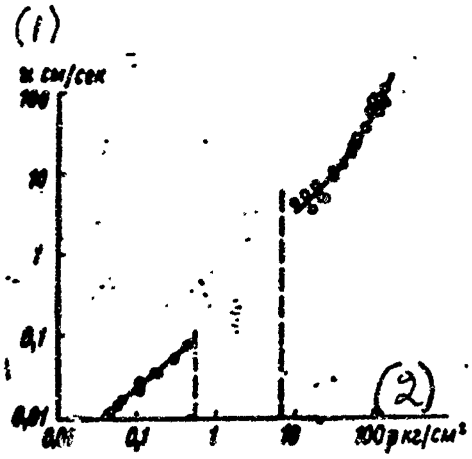

Fig. 4. Dependence of burning rate of nitroglycerine on pressure.
1) u, cm/sec; 2) p kg/cm^2.

From this it follows that in the case of NG an increase of pressure, while increasing the burning rate, not only does not promote the latter, but renders a reverse effect. This effect however is limited to a certain pressure range: above 11 atm burning is observed anew [6], but it proceeds, similarly to burning of NGL, in a turbulent regime with a constant rate, but one that is much greater than would correspond to normal burning (Fig. 4). An unusual phenomenon was observed during certain experiments with NG at increased temperature (near 100°): the flame penetrated, as it were, along one side of the wall of the tube to a great depth and the surface of the burning liquid became almost vertical. It is possible that this phenomenon represents pulsation of a very large period.

Thus, the main distinctions of NG from NGL are, first, the high burning rate, secondly, the turbulence of the latter which appears in NG at smaller pressure ($\frac{1}{2}$ atm), with which there is not yet a secondary flame, and, third, this turbulence leads not to accelerated pulsating burning, but to attenuation. The direct cause of attenuation is, apparently, an abrupt increase in heat loss during transition of burning to the turbulent regime, which leads to a strong increase of critical diameter. Experiments of G. N. Bespalov showed that with a turbulent regime, in spite of high speed of burning the critical diameter is much greater than during normal burning and grows quickly during lowering of pressure. If we extrapolate the obtained dependence $d_K = f(p)$ to one atmosphere, then the value of the critical diameter is equal to $\sim$15 cm. If we decrease turbulization by increasing viscosity of nitroglycerine by means of dissolving nitrocellulose in it, then critical diameter is greatly lowered, for example, at 15 atm from 4 to 0.5 mm.

Turbulization can be prevented also by decreasing tube diameter. It turned out that at atmospheric pressure the possibility of burning nitroglycerine can be ensured not only by increasing tube diameter, but also by using small diameters for it (from 0.5 to 1.5 mm), in spite of the fact that with small diameters the specific surface of heat drain is increased. This again shows that the main factor in the increase of heat loss during attenuation of burning NG in the area of low pressures is the appearance of turbulization.

By using a tube, sufficiently large diameter, for example, 20 cm, it would have been possible, apparently, for NG, as was observed for NGL, to achieve combustion at all pressures, starting from a low limit, equal to several millimeters of mercury, at first normal, and then turbulent. A check of this conclusion was not accomplished since it would have required using quantities of NG too large and dangerous under laboratory conditions.

Disturbance of Normal Regime of Burning of Pentaerythritetetranitrate (PETN)

The appearance of turbulence before burning is natural to imagine in the case of burning of liquids. However, if a solid melting substance burns, then part of the front heated layer is in liquid state. Experiments conducted with PETN showed that at low pressures, when thickness of heated layer and its melted part was relatively great, the effect of turbulization could develop. In determined conditions of the experiment (d = 7 mm, t° = 100°) PETN is capable of burning at atmospheric pressure. However with an increase of pressure to 1.5 atm burning is stopped. The ability of this explosive to burn appears again only at significantly larger pressures —from 16 atm.

Attenuation of burning in pressure range 1.5--16 atm can be connected with the onset of turbulization in the melted part of the heated layer. With a relatively small burning rate of solid substance (0.031 g/cm^2 sec at atmospheric pressure) thickness of the heated layer is comparatively great. In these conditions PETN will conduct itself similarly to liquid NG. The distinction lies in the fact that, at increased pressures, when NG burns in turbulent regime with great speed, for solid PETN increased speed, corresponding to turbulent regime, is not observed. This is not surprising, since at great pressures, more accurately with corresponding high speeds of burning, the thickness of the heated, melted layer of PETN becomes so small that turbulence cannot be developed in it.

Experiments with liquid PETN at 140° showed that at pressure of about 8 atm its burning changes into a turbulent regime with a corresponding strong increase in speed.

One should add that both in the case of NG and in the case of PETN attenuation is observed at relatively low speeds of burning. It is possible that turbulization within the limits of the heated layer starts earlier that it is propagated in cold layers of liquid and is manifested in the macro-irregularity of the process of burning.

Effect of Mobility of Liquid On Disturbance of Normal Regime of Burning

A decrease in the mobility of a liquid, in particular an increase in its viscosity by means of dissolution in it of a small quantity of high-polymer substance (for example, nitrocellulose or polymethylmethacrylate) hampers the appearance of turbulence and also more or less significantly increases the pressure range, in which normal burning is observed. For NGL, gelatinized by collodion (97:3), —see Fig. 1 — normal burning was observed in all the studied pressure range (to 150 atm), while burning of liquid NGL changed into a turbulent regime at 20 atm.

In the same way gelatinization of NG affects its ability to burn. The greater the viscosity the higher the pressure at which this explosive loses its ability to burn; with a significant increase, a pressure range in which the substance is not capable of burning is not observed.

It is interesting that an increase in viscosity of the liquid leads to some deceleration of burning, the more significant, the stronger the viscosity is increased and, apparently, the greater the burning rate of liquid. This lowering of speed is also observed if the polymer (nitrocellulose) has a high speed of burning than the liquid in which it is dissolved.

Not excluded is the fact that in the case of low-viscosity liquid because of boiling, the surface of the front of burning obtains a certain microrelief, expressed to a higher degree than in the case of viscous gelatin. It is also possible, however, that in the studied conditions of burning an essential role is played by diffusion in condensed phase [1], the speed of which is decreased with an increase in viscosity.

Disturbance of the normal regime of burning and its stabilization by an increase of viscosity were observed for other individual liquid substances, in particular nitrates of alcohol. Whittaker /10/ et al. have described this phenomenon for many two- and polycomponent solutions of fuels (2-nitropropane, nitrile of sebacic acid) in oxidizers (nitric acid nitrogen tetroxide) and associated it with the fact that during evaporation of burning liquid its drops are carried away by outflowing vapor. These investigators studied the effect of viscosity, vapor

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[1] Due to preeminent detachment by nitro ester of nitric oxides and their transition to the gaseous phase the burning surface of liquid is impoverished by the oxygen which ~~occurs~~ because of diffusion ~~of~~ the nitric oxides released in the deeper layers of the substance.

tension of the fuel, and the diameter and form of the tube. On increase in viscosity, attained by dissolution of polymethylmethacrylate, decreased the burning rate, which moved toward a certain limit, and increased pressure of transition to the turbulent regime. This pressure somewhat decreased with an increase of tube diameter. At 14.6 atm a mixture of 2-nitropropane with 97% nitric acid burned with speed of 0.114 cm/sec; with 0.1,0.5 and 0.75% polymethylmethacrylate in this mixture the burning rate was 0.079, 0.076 and 0.074 cm/sec, and critical pressure of transition of burning to turbulent regime of liquid and gelatinized mixtures of nitropropane and nitric acid constituted 76, 83, 117 and 130 atm respectively.

Experiments with gelatinized liquids allowed us to explain also the question as to whether the appearance of pulsation of burning is caused by secondary flame. In the case of gelatin this flame appears with pressure and is located even somewhat nearer to the surface than during burning of liquid; pulsating burning is observed in the first case and is absent in the second even while the secondary flame is located quite near the surface of the burning substance. The absence of a straight connection between appearance of secondary flame and transition of burning to turbulent regime is confirmed also by the fact that for certain liquids, for example for NG, this transition occurs at pressures so low that there is no secondary flame as yet.

Theory of the Phenomenon

Independently of experimental investigations, L. D. Landau [7] considered theoretically the burning of liquid, occurring by means of its transition into vapor and chemical reaction in vapor. He showed that the front of burning is stable only in a case where the burning rate does not exceed a certain critical value, which is determined by the formula

$$u_{\text{кр}}=(4\alpha_{\text{ж}}g\rho_{\text{г}}^{2}\rho_{\text{ж}})^{1/4}, \qquad (1)$$

where $u_{\text{кр}}$ —critical value of mass burning rate;

$\sigma_{\text{ж}}$ —surface tension at the boundary between liquid and its saturated vapor.

g —gravitational acceleration;

ρ_{r} —density of gaseous products of burning;

$\rho_{\text{ж}}$ —liquid density.

The conclusion of L. D. Landau is that during burning the horizontal surface of liquid becomes unstable, and its distortion tends to grow in amplitude. This growth however, is hindered by gravity and the force of surface tension. Up to a value of speed corresponding to expression (1), these forces are able to hinder the development of turbulence; at large values of speed it sets in.

Formula (1) can be presented [5] in the form

$$u_{\text{кр}} = \gamma \frac{P}{M} \cdot \rho_{r}^{1/2} \rho_{\text{ж}}^{3/4}, \tag{2}$$

where P —parachor; M —molecular weight of liquid; γ —constant, equal in CGS system to 7.91.

Magnitude P/M for organic liquids changes within narrow limits, just as the density of the liquid; also density of gases at constant pressure only relatively slightly changes. Therefore formula (2) approximately can be presented in the form

$$u_{\text{кр}} = \beta p^{1/2}. \tag{3}$$

Turbulization of the front of burning can be prevented also by means of increase of viscosity of liquid. V. G. Levich [8] showed that critical value of burning rate is connected with viscosity by the formula

$$u_{\text{кр}} = (3\sqrt{3} g \eta \rho_{r}^{2/3} \rho_{\text{ж}}^{1/3})^{1/4}, \tag{4}$$

where η —viscosity of liquid.

Thus, if surface tension and gravity are not able to prevent disturbance of front of burning, turbulization still cannot appear, if viscosity of liquid is sufficiently great. However, the necessary magnitude of viscosity is sufficiently high and, for example, for the burning rate inherent in NG at atmospheric pressure, constitutes about 1 poise, i.e., three times more than its viscosity at room

STOP

temperature. Therefore in order that the stabilizing effect of viscosity be developed during the burning of nitrates of alcohols it is required to increase artificially, for example, the dissolution of high-polymer substances.

The formulas of L. D. Landau and V. G. Levich explain the regularities determined by experiment. Since the main factor determining the onset of turbulent regime is the magnitude of rate of burning at a given pressure, then it is natural that first of all (i.e., at the least pressure) turbulization is developed on burning NG, the most readily combustible, and then **methylnitrate** NGL, and diglycoldinitrate. It is apparent that the effect of pressure and initial temperature promotes the appearance of turbulence. With an increase of pressure the critical value of the burning rate grows (Fig. 5), but relatively slowly, proportionally to the square root of the pressure; the speed of burning, as experiment shows, is increased approximately proportionally to the pressure and naturally at a certain pressure becomes more than critical.

One should indicate that transition of burning to turbulent regime should also occur because as the pressure at which burning proceeds approaches the critical value (in the usual physicochemical meaning of this term), the surface tension is decreased to zero and in conformity with formula (1) the critical value of speed also falls to zero. Critical pressure, as experiment shows, for many organic liquids lies near 50 atm.

From the formulas and from the graph of Fig. 5 it is clear that transition of burning to turbulent regime promotes also, as we saw in the example with NGL, an increase of initial temperature of substance, since it increases the burning rate; critical value of speed virtually does not depend on initial temperature.

In agreement with theoretical conclusions and the observations concerning the effect of viscosity on the considered phenomenon in the sense that the burning of slow-burning NGL is easily stabilized, but quick-burning NG requires large contents of dissolved nitrocellulose to support the normal regime of burning.

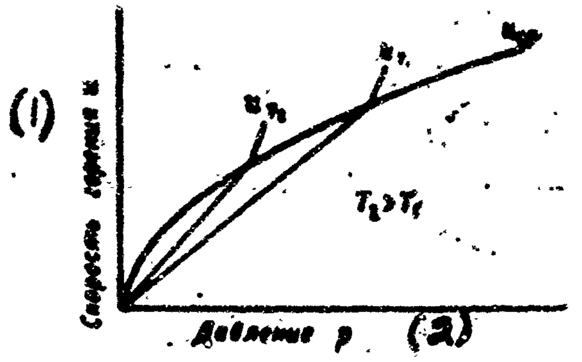

Fig. 5. Dependence of burning rate and its critical (according to Landau) value on pressure and initial temperature.

1) Burning rate u; 2) Pressure p.

The striking influence of the decrease of mobility of a liquid on its stability of burning is illustrated in the experiments of B. N. Kondrikov (see page 443) with NG, in which mobility of liquid was decreased by adding to it lead azide. A mixture of equal (by weight) quantities of NG and lead azide at pressures from 6 to 40 atm burns, as a rule, without exploding while NG itself when ignited in a range from 6 to 11 atm dies out or gives an explosion, and lead azide detonates at all pressures. Moreover, at those increased pressures, with which NG starts to burn anew, but now in turbulent regime, i.e., with great speed, the addition of lead azide, obviously hampering turbulization, sharply (approximately twice) lowers the burning rate. This is observed during burning of liquid NGL with lead azide in the area of turbulent regime, i.e., at pressures higher than 20 atm.

The Connection Between Turbulent Burning And Transition of Burning Into an Explosion

Decrease of mobility of liquid, in particular, by means of increasing its viscosity is an effective method of preventing the transition of burning from normal into turbulent regime. This method is used in the contemporary powder industry, ensuring stability of burning of smokeless powders in low-volatile solvent. Preventing the appearance of turbulent burning is also an important factor in preventing its transition into explosion. Experiments set up in due time [1] on burning of liquid nitrates (NG and NGL) in an iron pipe with a closed disk, exploding at a certain pressure, showed that the burning of these liquids, with a small durability of disk, easily changes into explosion. At the same time gelatinized NG containing only 7% nitrocellulose burned steadily throughout the studied range of disk durabilities (to 1200 kg/cm^2, charge 200 g).

It is known, however that when igniting strongly heated nitrogelatin (9) it explodes; a similar explosion occurs also when determining its flash point.

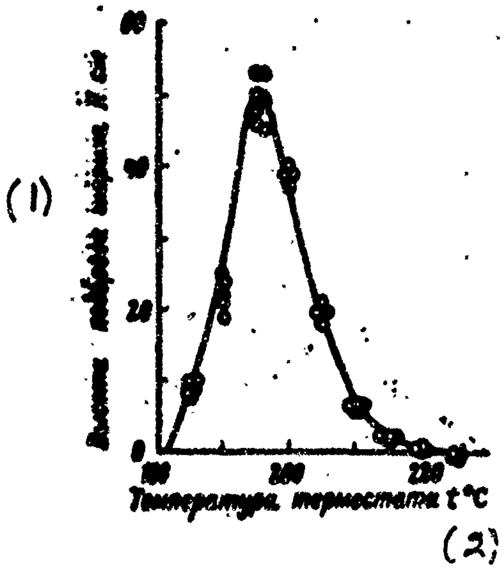

Fig. 6. Dependence of flash intensity of 50% nitroglycerine gelatin on temperature of thermostat.

1) Height of bounce of ball H cm; 2) Temperature of thermostat t°C.

Besides that, experiments showed that it is possible to greatly increase the intensity of flash even in the case of gelatin, containing much more (to 50%) nitrocellulose. These experiments of B. N. Kondrikov and I. V. Babaytsev were set up in the following manner (see page 515). A small weighed amount of gelatin (0.02 g) was introduced into the test-tube, located in the thermostat. The intensity of the flash was determined depending upon the temperature of the thermostat. The measure of this intensity was judged by the height of the bounce of the ball, freely covering the mouth of the test-tube. The character of the established dependence is unusual (Fig. 6) and is explained in the following manner. At low temperatures only slow decomposition occurs, with which the speed of gas formation is so small that the ball does not bounce; at high temperatures, before gelatin has time to heat, ignition quickly occurs; burning proceeds on the macrosurface of the piece and speed of gas formation is again insufficient to bounce the ball. At intermediate temperatures of gelatin it can be heated to ignition. However not only this heating alone increases the burning rate. As a result of chemical processes, in particular depolymerization of nitrocellulose, the viscosity of gelatin is lowered so much that its burning occurs with intense turbulization and dispersion of substance by escaping gases. All this leads to such a strong development of the burning surface that the flash takes the character of an explosion, splitting the test-tube and strongly bouncing the ball, similar to that, which happens under similar conditions with ungelatinized, NG.

Thus, transition of burning of liquid to a turbulent regime considerably favors the possibility of explosion. This is not surprising. The main distinction of detonation from normal burning is that with it the reaction takes place under much greater pressure and in the form of burning suspended matter of particles of substance which also establishes a much higher speed of process. Thus for realization of transition of burning into explosion pressure should grow and suspended matter of the explosive substance should be formed. However, it is sufficient only to form suspended matter: if total surface of its burning particles, i.e., the surface of burning, is sufficiently great, then pressure will be increased automatically.

This refers, in particular, to the burning of NG. Even in the usual laboratory conditions of a test at flash point it gives, as is known, an intense explosion. Even more we expect explosion at appearance of flash of NG in industrial conditions, where dimension of the warm-up zone can be much larger. Therefore because of the ease of developing turbulence of burning and the low pressures, with which it starts, self-ignition of NG in industrial conditions practically always leads to explosion.

The Double Influence of Pressure On Transition of Burning Into Explosion

The essential factor of transition of burning into explosion is considered to be, and not unfounded, an increase of pressure. If powdery substance burns, then an increase of pressure to a definite magnitude leads to penetration of hot products of burning into the depth of the charge and if relatively quickly there is formed a sufficiently thick layer of burning suspensions, then this can lead to transition of burning into explosion. In the case of liquids an increase of pressure, as we have seen, leads to the appearance of turbulence, which in its turn promotes transition of burning into explosion. Apparently, for such transition onset of turbulization is more favorable at low pressures, when speed of formation is great, and linear speed of its combustion is small and there occurs, therefore, an accumulation of particles or drops of the substance.

Another phenomenon is possible. With excessively intense turbulization cooling of flame by liquid proceeding into it becomes too great and burning is stopped. However, if during attenuation a large quantity of liquid was heated also to a sufficiently high temperature, then in it can be developed self-accelerated decomposition, which can lead to a surpassing of heat gain over heat losses and to flash, and consequently, in the case of NG, also to explosion. Attenuation and explosion in these conditions are neighbors and turbulization can lead to explosion not by itself, nor from increase of burning rate, but through formation of a sufficiently large volume of heated substance, in which thermal explosion can be developed. Local explosion of NG after being heated during attenuation leads to explosion of all the remaining "cold" part of the substance. Explosion of such a type is easy to realize, by creating artificial local warm-up of surface layer of liquid, with a heated spiral, introduced into the NG to a certain depth (1.5—2mm). When the spiral is on the surface, then igniting causes only a weak flash, accompanied by spraying of liquid and leading neither to burning, nor to explosion.

Under the conditions of the described experiments on igniting by spiral, an increase of pressure, preventing attenuation, can render a stablizing effect on burning. This effect is graphically illustrated by the experiments B. N. Kondrikov with mixtures of liquid nitrates with azide of lead and burning them in the area of moderately increased pressures.

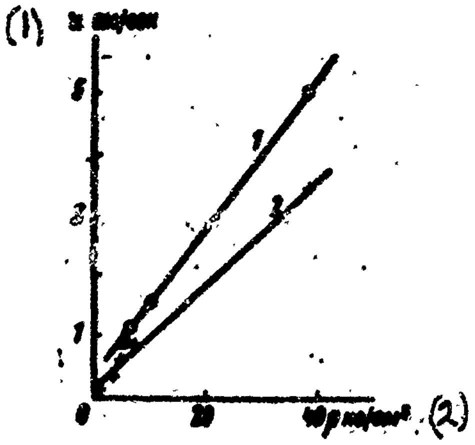

Fig. 7. Dependence of burning rate of mixture of nitroglycerine and azide of lead (50:50) on pressure.

1) mixture with nongelatinized NG, 2) mixture with gelatinized NG.
1)u, cm/sec; 2) kg/cm^2.

Thus, a mixture of equal (in weight) quantities of NG and azide of lead at 3.7 atm gave an incomplete explosion, at 4.9 atm there occurred attenuation, and at 5.4 and higher pressures (to 40 atm) burning was observed, as a rule, without transition into explosion (Fig. 7). An analogous picture is observed also for weakly gelatinized NG; it, by itself, thanks to increased viscosity, is capable of stable burning; addition of azide of lead (50%) deprives it of this ability at low pressures --igniting leads to attenuation; an increase of pressure to 3 and more atmospheres returns its ability to burn.

This refers also to mixes on the basis of NGL (Fig. 8) and diglycoldinitrate; with this the less the burning rate of nitrate, the bigger the pressure, starting from which its ability to burn is restored.

These observations are explained naturally based on the idea that transi urning into explosion is connected with the scope of chemical reaction when ig- niting a layer of substance of a certain critical thickness. Explosion of this layer, more accurately the suspensions of particles of the substance, which form during development of reaction in it, if it leads to the appearance of a drop in pressure of sufficient magnitude, causes explosion of the remaining part of the charge. If this drop is insufficient, then attenuation occurs or at small amplitude pulsating burning appears. Increase of pressure under the conditions of the described experiments hampered thickening of reacting layer to a thickness necessary for appearance of explosion.

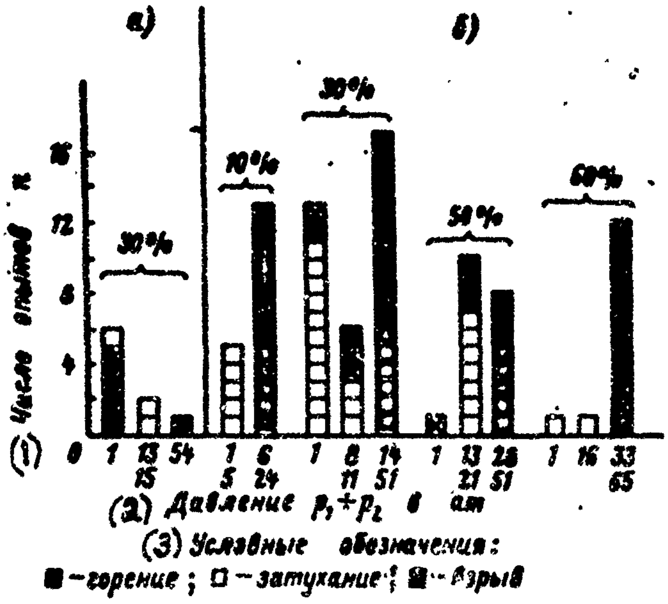

Fig. 8. Effect of composition, pressure and method of igniting on behavior of mixtures of weakly gelatinized nitroglycol and azide of lead.

a—igniting directly by spiral, b—igniting by means of a layer of weakly gelatinized NGL. Every square on the graph corresponds to one experiment. Numbers, located along axis of abscissas, signify pressure (or pressure range), with which experiments were produced. Numbers by brackets —contents of azide of lead in its mixture with gelatinized nitroglycol.

1) Number of experiments; 2) Pressure $P_1 \div P_2$ in atm; 3) Condition designations: ■burning; □attenuation; ■ explosion.

Conclusions

Dependencies of burning rate on pressure and initial temperature for liquid substances, in particular nitrates of alcohol, differ because of turbulization of the front, setting in under definite conditions of burning, from those, which are observed for solid substances. The main factors, determining transition of burning into a turbulent regime, are the magnitude of the burning rate and the pressure. Turbulization leads to a sharp increase in the quantity of liquid, proceeding into the zone of burning which can at low pressures cause attenuation of it, but at high pressures —strongly increases the quantity of the burning substance. The appearance of turbulent burning during an increase in pressure can lead to transition of the latter into an explosion, especially at low pressures. In known conditions an increase of pressure can stabilize burning.

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Chapter 3 Article 28

Pages 430 - 442

K. K. Andreyev and G. N. Bespalov

28. On the Burning of Nitroglycerine

With respect to burning ability nitroglycerine is distinguished from other nitro esters studied from this point of view by certain peculiarities [1]. In ordinary conditions of laboratory experiment (igniting of an incandescent spiral at room temperature and atmospheric pressure in a glass tube several millimeters in diameter) nitroglycerine does not burn. In order to obtain burning it is necessary to conduct the experiment at lowered pressure (½ at). Burning, but already in turbulent conditions, is observed also at pressures (p) greater than ~11 at [2], and besides, its speed (u) is an order greater than it was possible to expect, extrapolating the dependence u on p, obtained in the area of lowered pressures.

Loss by nitroglycerine of burning ability at pressure above ½ at was explained by the transition of burning to turbulent conditions. In the area of low pressures, when chemical transformation during burning takes place with incomplete heat liberation, constituting only nearly half of the possible maximum, taking place as a result of the turbulence of a large quantity of liquid in the relatively cold and hardly-closed zone of burning stops the chemical reaction, since thermal loss becomes too large. From this explanation it follows that by decreasing relative thermal loss, for example by increasing the diameter of the tube, it would have been possible to hamper attenuation, and in the limit with a sufficiently large diameter, in general to prevent it. Burning of nitroglycerine would be then similar to burning, for example, of nitroglycol. As it is known [1], in the last case are observed two pressure areas -- normal (to~ 20 at) and turbulent (above 20 at) burning -- without a range of pressure, in which burning is not spread.

If this is so, then attenuation of burning of nitroglycerine with an increase of pressure can be considered as the result of a significant increase of the critical diameter of burning upon transition to turbulent conditions. By increasing the diameter of the tube in this case, it would have been possible to increase pressure of attenuation and, finally, to raise it 11--15 at, when burning in turbulent conditions is spread stably with a diameter of the tube of 5 mm. Probably, it would be even sufficient to increase pressure of attenuation of normal burning to a lesser, than shown, magnitude, since it, during burning in turbulent conditions, is lowered with an increase of diameter. Thus, enlargement of the diameter of the tube would approach both -- the lower and upper limits of the range of absence of burning by pressure and should lead to their blending, i.e. to the disappearance of this interval.

Side by side with the shown version, that it was possible to conditionally designate as the transformation of nitroglycerine into nitroglycol; another is also possible -- transformation of nitroglycol into nitroglycerine. Having created the conditions of reinforced heat supply, it is possible to expect also for nitroglycol ceasing of burning upon transition of the latter to turbulent conditions. These conditions can be the small diameter of the tube or, better, finding it instead of air in water or other liquid.

A check of these considerations also was one of the problems of this work. The solution of it appeared, however, hampered by the circumstance that the diameter, starting from which nitroglycerine is capable of burning in the whole range of pressures, apparently, is so great, that it makes the experiments in laboratory conditions unsafe.

In order to avoid application of large charges; we went in the direction of an increase of viscosity of nitroglycerine by means of dissolution in it of nitrocellulose (gelatination). The increase of viscosity hampers turbulence and subdues its results [1].

Critical Diameter of Burning of Liquid Nitroglycerine At Various Pressures

For determination of critical diameter of burning, nitroglycerine was poured into a conical glass tube with angle at the peak not more than 10°. In order to ensure constant conditions of heat supply, the tube was placed in a glass with water. Experiments were conducted in a cylinder of constant pressure in an atmosphere of nitrogen. Igniting was realized from the wide side of the conical tube by an incandescent Nichrome wire. The critical diameter of burning (d_c) was considered as the diameter, below which burning was not spread.

As the experiments showed, the critical diameter of burning of nitroglycerine in the area of increased pressures does not depend on whether the tube with nitroglycerine is in water or in gas, that apparently, can be explained by the great burning rate in these conditions, in consequence of which the relative magnitude of thermal loss from the quickly moving zone of reaction does not change due to a change of the coefficient of heat radiation of the external surface of the glass tube.

The results of experiments at increased pressures (100—13 at), when nitroglycerine burns in turbulent conditions, show that the critical diameter of attenuation is greatly increased upon lowering of pressure. The curve, describing this growth (Fig. 1, curve 1), can be presented by the equation $d_c = \frac{145}{p^{1.31}}$ where d_c — critical diameter in mm, and p — pressure in kg/cm^2. Upon transition from 100 to 13 at, d_c increases from 0.35 to 3.5—5 mm. If the obtained dependence is fulfilled also at a further decrease of p, then the critical diameter at atmospheric pressure should constitute 14.5 cm.

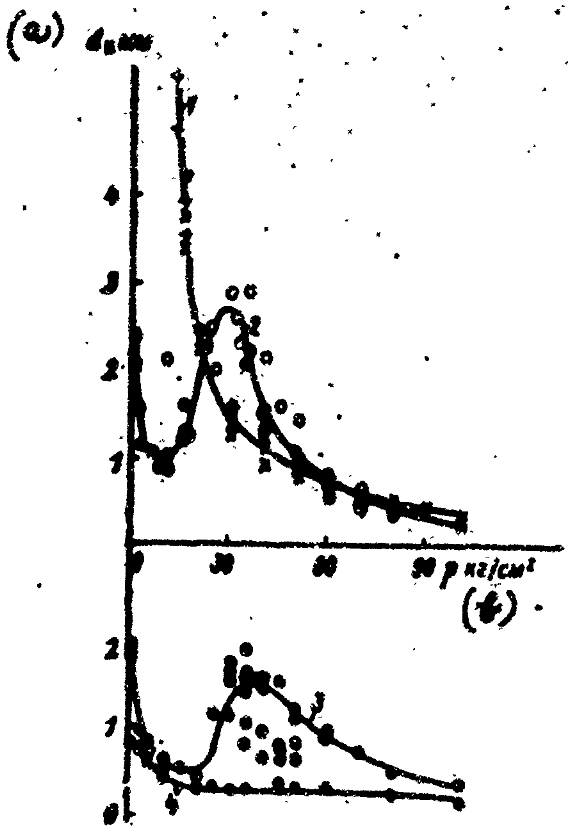

Fig. 1. Dependence of critical diameter of burning (d_c) of nitroglycerine and its gelatin on pressure (p) in the range above atmospheric pressure.
1 — nitroglycerine (+ — in air environment; — in water environment), 2 — 3.2% gelatin, 3 — 5% gelatin, 4 — 8.5% gelatin. (a) d_c mm; (b) p kg/cm^2.

Fig. 2. Dependence of critical diameter of burning of nitroglycerine on pressure in the range 150—1000 mm Hg.
(a) P mm Hg; (b) d_c mm.

In a range of pressures below atmospheric, where burning takes place without visible pulsation, upon increasing p the critical diameter increases[1] (Fig. 2). At p = 150 mm Hg the critical diameter constitutes 2.5 mm, at 390 mm — ~ 7 mm and at 1050 — 10 mm.

This circumstance is somewhat unexpected, since usually with an increase of pressure, i.e. an increase of the burning rate, the thermal losses, and with them the critical diameter, are decreased. Apparently, established by the data of the experiments, the original dependence is stipulated by the fact that with the caused growth of pressure by increase of the burning rate is reinforced by turbulence of its front, which also increases thermal loss. This reinforcement thermal loss due to the appearance of turbulence is greater than their decrease due to an increase of the burning rate. Thus an increase of critical diameter is a more sensitive index of the beginning of turbulence of burning, than an increase of its speed and appearance of pulsation. The possibility of observation of the latter, for example, in photographic registration of the process depends on the resolving power of the apparatus. Usually pulsation is fixed only in developed turbulence. In favor of these considerations is the circumstance that the critical diameter of gelatinized nitroglycerine, during the burning of which turbulence is basically suppressed in the same area of pressures in comparison to an ungelatinized substance is much less and is decreased with the increase of pressure: the critical diameter of 3% nitroglycerine gelatin constitutes at atmospheric pressure approximately 2 mm, and

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[1] Methodically these experiments were set up not as the determination of diameter of attenuation during burning in conical tubes, but as determination of pressure of attenuation during burning in cylindrical tubes of different diameter under slowly increasing pressure. In these experiments on determination of critical diameter at pressures below atmospheric, the tube with nitroglycerine was not placed in water, since this led to too large d_c (more than 12 mm). In all remaining cases, described below, the tube was placed in water.

nitroglycerine in these conditions does not burn even at a tube diameter equal to 12 mm.

One should indicate that in experiments on determination of critical conditions of burning very "soft" igniting is necessary. As burning of nitroglycerine was obtained even at atmospheric, however, only with one of the different tested methods of ignition, and namely igniting at lowered pressure with its subsequent growth to 1 at. Apparently, the usual methods of igniting promote the appearance of well-developed turbulent conditions of burning, with which the critical diameter is much greater than during normal burning.

Subsequent experiments[1] showed that the dependence of the possibility of burning of liquid nitroglycerine on the diameter of the tube (d) is more complicated (Fig. 3). If at low pressures (140--150 mm Hg) is observed only the usual lower limit of the diameter, obviously stipulated by heat losses of normal burning, then at large pressures, for example, at 1 at, burning, stably taking place at small diameters, stops being spread at somewhat larger values and again acquires this ability upon further increase of diameter. With this, the burning rates in tubes of small and large diameters are approximately identical and equal to 0.14--0.18 cm/sec. Correspondingly the experimental method of establishment of both critical values of diameter (d_1 and d_2) was different. For determination of the first of them nitroglycerine was ignited how usual in a tube tapering downwards; burning was stopped after achievement of d_1; for determination of the second limit nitroglycerine was ignited in a tube expanding downwards; burning was stopped upon reaching d_2. Another possible version of determination of the dependence $d = f(p)$ and d_2 included determination of pressure of attenuation during burning of the substance in cylindrical tubes.

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[1] In this series of experiments nitroglycerine was applied with temperature of hardening 11.8°. The results, obtained with this nitroglycerine, quantitatively were somewhat distinguished from that described above, but the general picture was maintained.

By this method curves were also obtained, shown in Fig. 3.

The described dependence of d_c on p could be explained by the fact that at pressure of approximately 1 at the burning rate is already sufficiently great in order to cause significant turbulence.

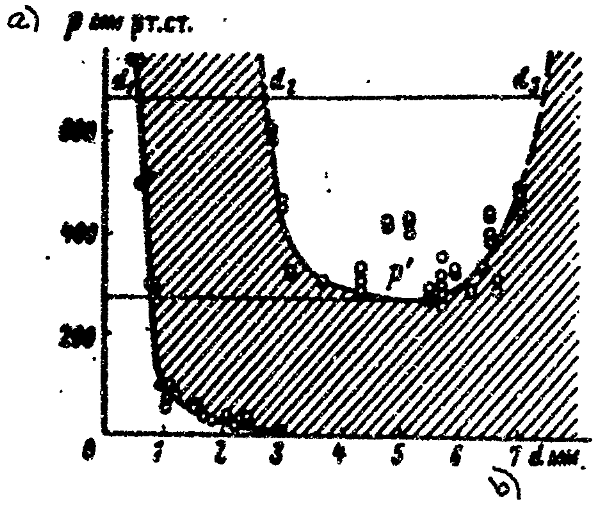

Fig. 3. Area of burning of nitroglycerine at small pressures (cross-hatched)[1]. a) p mm Hg; b) d mm.

At small diameters, however, this turbulence cannot be developed and burning does not die out; increase of diameter decreases the stabilizing effect of the tube, turbulences causes amplification thermal loss, and burning dies out. At further increase of diameter of tubes, relative thermal losses are decreased, and burning at a certain diameter of d_3 again becomes possible. As confirmation of the described explanation serves again the fact that at pressure of 1 at for gelatinized nitroglycerine a range of diameters, in which burning is not spread, is not observed.

Upon lowering pressure, d_1 naturally is increased; d_2 also increases, since at a lower burning rate its inclination towards autoturbulence is lowered, and stabilization of the process is realized even at a relatively large diameter; d_3 is decreased due to the fact that because of lower turbulence (less than the burning rate) the thermal losses stipulated it are decreased. At a certain

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[1] At pressures below ~ 20 mm Hg d_c was not determined.

sufficiently low pressure p', d_2 and d_3 become identical, and the range of diameter, in which burning is not observed, disappears. From these data, incidentally, follows a paradoxical conclusion: in order to interrupt burning of nitroglycerine by means of passing it through a multichannel barrier it is not expedient to make the channels too thin, since in this case turbulence can be suppressed.

Critical Diameter of Burning of Gelatinized Nitroglycerine At Various Pressures

Gelatination of nitroglycerine by dissolution in it of nitrocellulose leads to a certain deceleration of burning, and mainly greatly hampers the appearance of turbulence due to a sharp increase of viscosity of the solution. In accordance with this, the area of turbulence during burning of gelatin ($\sim 3.2\%$ by weight of nitrocellulose) is displaced in the direction of large pressures, and the curve $d_c = f(p)$ takes on an original form (Fig. 1, curve 2). In the area of low pressures (1—10 at) the critical diameter is decreased with the increase of pressure — obviously due to an decrease of relative thermal loss because of the increase of burning rate. However in the range from 10 to 30 at the critical diameter grows and, for example, at 30 at is significantly greater than at 5 at. This growth should add to the increase of thermal loss due to the appearance of turbulence[1], the influence of which in this case is stronger, than the influence of the growth of the burning rate. At a further increase of pressure from 30 to 100 at the critical diameter is decreased, apparently, because in this region of pressures the influence of growth of burning rate, and possibly also the increase of its temperature (due to the transition to combustion up to N_2 instead of NO),

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[1] The originality of this turbulence is the fact that in causing the increase of critical diameter, it is not accompanied by an increase of the burning rate. Such an increase for 3% gelatin appears, apparently, only at much greater pressures (approximately 300 at), when in a series of photographs sometimes a sudden strong increase of burning rate was observed (see Table 2, photo 10)

obtains a predominant value.

It is interesting to compare the curve for gelatin with the curve for nongelatinized nitroglycerine (Fig. 1, curve 1). From 10 to 25 at the critical diameter of liquid nitroglycerine is much greater than gelatin, in spite of the fact that the speed of its burning is approximately 10 times more. This undoubtedly is the result of more intense turbulence in the case of a liquid nongelatinized explosive, stipulating greater thermal loss, and graphically illustrates the influence of this factor on critical diameter. From 25 to 50 at, conversely, d_c of nitroglycerine is already somewhat less than gelatin — this, apparently, is the result of the high speed of burning of the liquid. Experiments with more viscous (5% nitrocellulose) gelatin (Fig. 1, curve 3) showed, in general, a similar (with 3% gelatin) picture. In order to suppress turbulence by increasing viscosity (burning rate upon change of contents of nitrocellulose from 3 to 8.5% practically does not change — Fig. 4), it was necessary to increase the contents of nitrocellulose in nitroglycerine to 8.5%. In this case (Fig. 1, curve 4) a maximum on the curve $d_c = f(p)$ is not observed, however, on the graph is seen in the corresponding area of pressures a section of constancy of critical diameter.

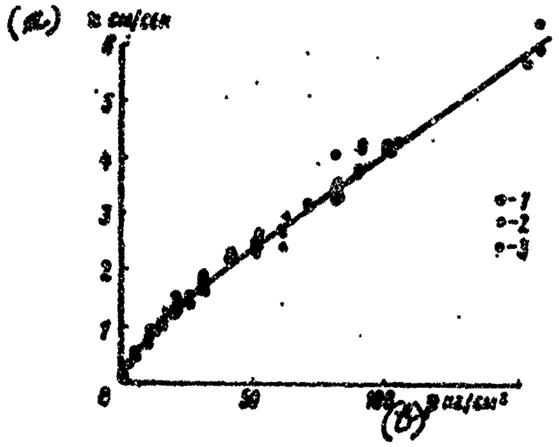


Fig. 4. Dependence of burning rate of nitroglycerine gelatin on pressure. 1—3.2%, 2—5%, 3—8.5%
(a) u cm/sec.; (b) p kg/cm^2.

In Table 1 are equations, describing the dependence of d_c on pressure for nitroglycerine, and also for nitroglycerine gelatin and certain other studied nitro esters and their mixtures.

Table 1

Dependence on pressure of critical diameter of burning of liquid and gelatin nitro esters and their solutions

1 Вещество	2 Интервал давлений ат.	* $d_к = f(p)$
3 Нитроглицерин	13—100	$d_к = \frac{145}{p^{1,3}}$
4 3,2%-ная нитроглицериновая желатина	1—10	$d_к = \frac{2,16}{p^{0,6}}$
	25—100	$d_к = \frac{3300}{p^{2,1}}$
5 5%-ная нитроглицериновая желатина	1—20	$d_к = \frac{2,21}{p^{0,6}}$
	50—100	$d_к = \frac{2140}{p^{3,0}}$
6 8,5%-ная нитроглицериновая желатина	3,5—21	$d_к = \frac{1,70}{p^{0,6}}$
	60—100	$d_к = \frac{17,8}{p}$
7 Нитрогликоль	2,5—21	$d_к = \frac{19,3}{p^{0,8}}$
	21—81	$d_к = \frac{36,2}{p^{1,2}}$
8 3%-ная нитрогликолевая желатина	1—21	$d_к = \frac{7,41}{p^{0,7}}$
	21—61	$d_к = \frac{17,4}{p}$
9 Смесь нитрогликоля с нитроглицерином (90 : 10)	1—20	$d_к = \frac{13,3}{p^{0,6}}$
	13—81	$d_к = \frac{145}{p^{1,4}}$
10 Дигликольдинитрат	16—81	$d_к = \frac{400}{p^{1,5}}$

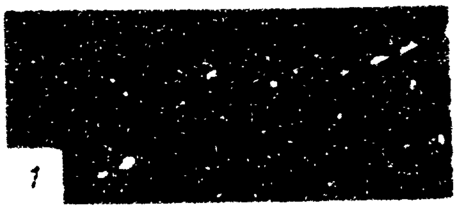
1) Substance; 2) Range of pressures, at; 3) Nitroglycerine; 4) 3.2% nitroglycerine gelatin; 5) 5% nitroglycerine gelatin; 6) 8.5% nitroglycerine gelatin; 7) Nitroglycol; 8) 3% nitroglycol gelatin; 9) Mixture of nitroglycol with nitroglycerine (90:10); 10) Diglycol dinitrate.

*NOTE: The English equivalent of the Russian d_k is d_c.

Table 2

Character of burning of different liquid and gelatin nitro esters and their solutions. Photographs obtained with the help of a photoregister.

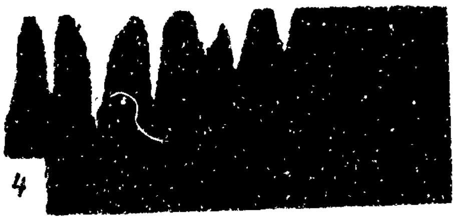
Nitro esters: the pressure at which their burning occurred and results of observation



1. 5% nitroglycerine gelatin, p = 6 at. Clearly noticeable frontal primary illumination

2. 3% nitroglycerine gelatin, p = 26 at. A certain distortion of the burning front and periodic approximation to it of a secondary flame is observed

3. 5% nitroglycerine gelatin, p = 42 at. Frontal primary illumination and much more bright secondary flame, separated from the first dark zone



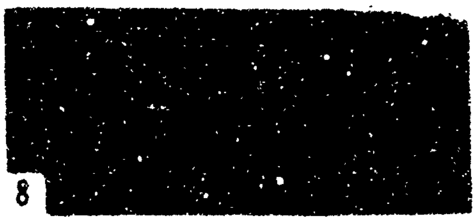
4. 10% solution of nitroglycerine in nitroglycol, p = 24 at. Starting in normal conditions, burning changes to turbulent conditions

5. 10% solution of nitroglycerine in nitroglycol, p = 16 at. Irregular distortion of the burning front -- pulsating burning

6. 10% solution of nitroglycerine in nitroglycol, p = 26 at. periodic turbulence with a frequency of 80 sec^{-1}

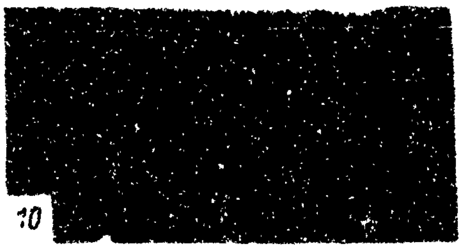
Table 2 (Continued)

7. Diglycol dinitrate, p = 81 at. Burning with great speed; at transition of burning from a tube of large diameter (4.8 mm) to a thick-walled capillary (1 mm) decrease of the burning rate and disappearance of secondary flame is observed



8. 10% solution of nitroglycerine in nitroglycol, p = 9 at. Multi-zone structure of primary flame

9. 5% nitroglycerine gelatin, p = 213 at. Gradual increase of speed by measure of burning of charge



10. 3% nitroglycerine gelatin, p = 361 at. Double sharp increase of burning rate

For illustration of the character of burning of the investigated substances and their mixtures in Table 2 are photographs of burning, obtained with the help of a photoregister.

Critical Diameter of Burning of Nitroglycol, Mixtures of It With Nitroglycerine And Diglycol dinitrate At Various Pressures

In Fig. 5 (curve 1) is shown the change of d_c with pressure for nitroglycol. In the entire area of pressure from 1 to 80 at the critical diameter is decreased from 13 mm at 1 at[1] to 0.4 mm at 80 at. However in the range pressures 10--20 at in those cases, when burning occurred with pulsation, attenuation occurred at a noticeably large diameter, in spite of the fact that the burning rate in these conditions was much larger.

In order to more clearly reveal the change of d_c upon transition of burning to pulsating conditions, experiments were continued with the application of solutions of nitroglycerine in nitroglycol (Fig. 5, curve 2). A 10% solution of nitroglycerine in nitroglycol burns somewhat faster than pure nitroglycol, and correspondingly a transition to turbulent conditions is observed at a somewhat smaller pressure ~ 15 at. Curve $d_c = f(p)$ has a maximum near this pressure; it is true that due to scattering of the points it is not very clearly expressed.

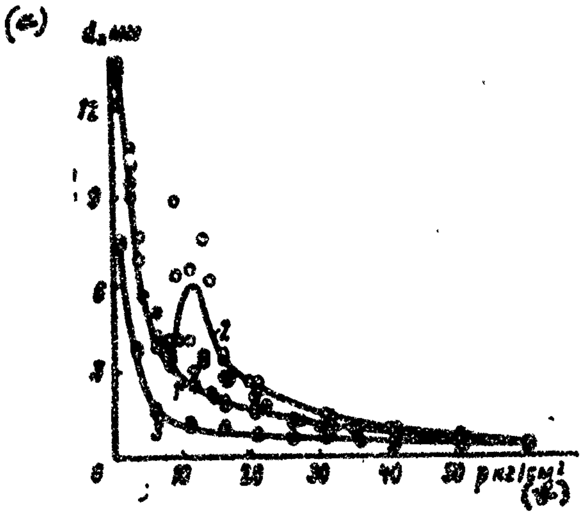


Fig. 5. Dependence of critical diameter of burning of nitroglycol, its mixtures with nitroglycerine (90:10) and 3% of nitroglycol gelatin on pressure. 1--nitroglycol, 2--10% solution of nitroglycerine in nitroglycol, 3--3% nitroglycol gelatin. (a) d_c mm; (b) p kg/cm^2.

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[1] If the tube is surrounded not by water, but air, then the critical diameter is significantly less (~ 1 mm).

An attempt was made also to obtain attenuation of burning of nitroglycol during transition to turbulent conditions. In usual conditions of the laboratory experiment for nitroglycol a range of pressure is not observed, dividing the area of normal and turbulent burning, in which burning could not be spread. The probable cause of this distinction of nitroglycol from nitroglycerine is the circumstance that for the first transition to turbulent conditions is observed at a high pressure (~20 at), when burning occurs already with full heat liberation and with significant speed, and the predomination of thermal loss above heat arrival is not realized.

Thermal losses may be increased by decreasing the diameter of the tube. This, however, did not lead to attenuation of burning, apparently, because the decrease of diameter hampered the appearance of turbulence similar to what was observed for nitroglycerine. Another possibility included the increase of temperature of the experiment, lowering, as it is known, the pressure of transition of burning to turbulent conditions. In addition, the tube with burning liquid was placed for amplification of heat supply in water at a corresponding temperature. In these conditions at 40° the transition of burning to turbulent conditions occurred at a pressure of approximately 8 at. In a significant part of the experiments conducted both in conical, and also in cylindrical tubes, attenuation was observed of burning at diameters of 4--10 mm (Fig. 6), and it was also observed in those cases, when burning started immediately in turbulent conditions.

Thus, attenuation of burning during transition to turbulent conditions may be observed also for nitroglycol, although for this explosive it is not so clearly expressed as for nitroglycerine.

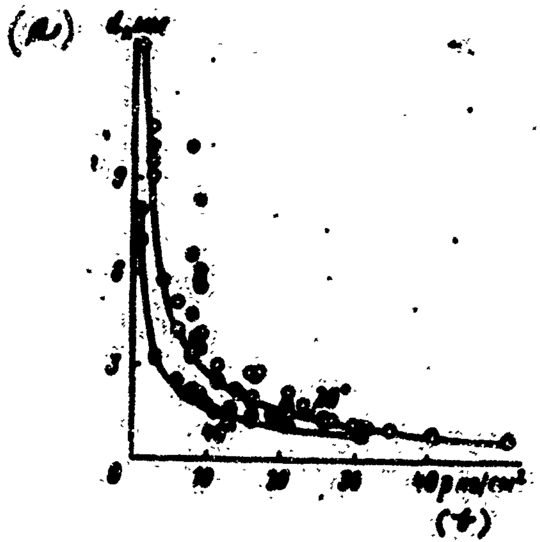

Fig. 6. Dependence of critical diameter of burning of nitroglycol on pressure at 40 and 20°. (a) d_c mm; (b) p kg/cm^2.

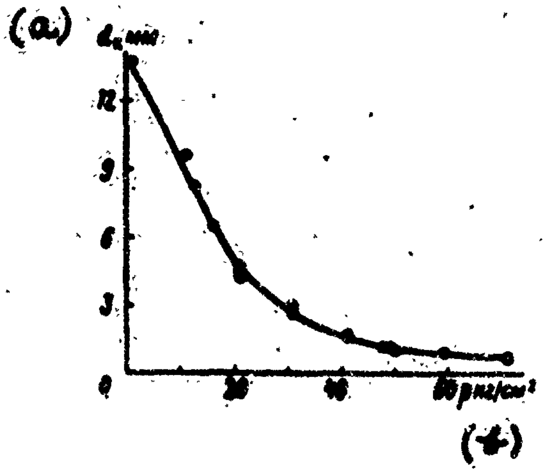

Fig. 7. Dependence of critical diameter of burning of diglycoldinitrate on pressure. (a) d_c mm; (b) p kg/cm^2.

The critical diameter of gelatin nitroglycol (Fig. 5, curve 3) is significantly less than for liquid at all pressures, possibly due to a decrease of the role of convection heat radiation; the distinction is specially great in the area of those pressures, where burning of the liquid changes to turbulent conditions.

The diameter of attenuation was determined also for burning of diglycoldinitrate. At atmospheric pressure the critical diameter is great (~14 mm) obviously in connection with the small burning rate[1]. At an increase of

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[1] In a tube, surrounded by air, the critical diameter at atmospheric pressure constitutes ~5 mm.

pressure it is decreased (Fig. 7). At a pressure above 55 at, burning of diglycol dinitrate changes to turbulent conditions, which, in particular, can be confirmed by the great burning rate in tubes of significant diameter (Fig. 8). However this speed is greatly decreased with a decrease of the diameter of the tube, obviously, due to its stabilizing influence. In connection with the fact that determination of diameter of attenuation was accomplished without simultaneous determination of the burning rate, it remains vague, whether to refer the value d_c at pressures above 55 at to turbulent or normal burning.

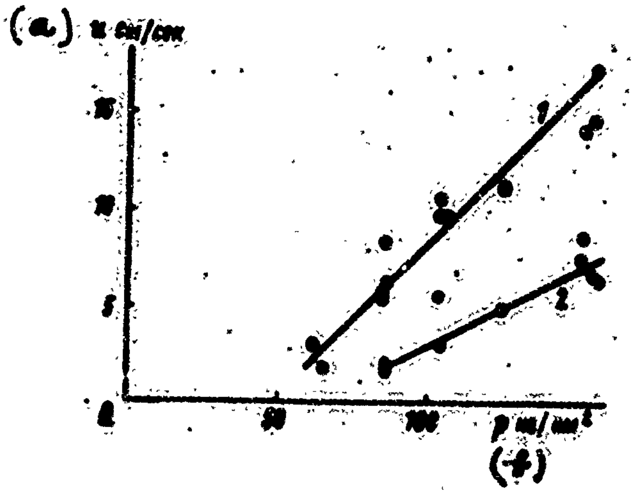

Fig. 8. Dependence of burning rate of diglycoldinitrate (at increased pressures) on pressure in tubes of different diameters. 1--5mm, 2--1 mm. (a) u cm/sec.; (b) p kg/cm^2.

Conclusions

1. Burning of nitroglycerine in liquid and gelatin nitrocellulose form and certain other nitro esters in the range of pressures 0.01--100 at was investigated.

2. Critical diameter and burning rate at atmospheric pressure for investigated nitro esters are:

	d_c in mm	u in cm/sec
Nitroglycerine....................	0.5	0.14
Nitroglycol......................	1.0	0.030
Diglycoldinitrate................	5	0.012

3. In the range of pressures 20—100 at the critical diameter of burning of indicated nitro esters is decreased at an increase of pressure according to the law $d_c = \frac{A}{p^n}$, where n is included between 1.15 and 1.48.

4. Transition of burning of liquid (nitroglycerine, nitroglycol) to turbulent conditions leads to a large increase of critical diameter.

5. Small diameters of the tube stabilize burning of nitroglycerine, hampering transition from normal to turbulent conditions; therefore in known conditions it is possible to observe three critical values of diameter: d_1 — the smallest, with which normal burning is possible, d_2 — the largest, above which the appearance of turbulence leads to attenuation due to an increase of thermal loss on the outside, and d_3 — above which burning again becomes possible due to the decrease of relative surface of heat supply. At atmospheric pressure the critical values of diameter constitute correspondingly 0.5; 2.6 and 7.5 mm.

6. Increasing the viscosity of nitroglycerine by means of dissolution in it of a high polymer (nitrocellulose), hampering turbulence, decreases the growth of the critical diameter (upon transition of burning to turbulent conditions), and at sufficient viscosity — eliminates it.

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Tape No. MT 63-254

Chapter 3, Article 29

Pages 443 - 456

B. N. Kondrikov

29. On The Burning of Mixtures of Initiating Explosives And Liquid Nitro Esters

The main peculiarity of initiating explosives consists in the fact that burning them changes into detonation under such conditions (small openly located charge, usual pressure and temperature), in which explosives of other classes burn stably and smoothly. The causes of this distinction are not completely clear. One of them, obviously, is the high speed of burning of initiating explosives, attaining at atmospheric pressure tens of centimeters per second. However this cause, apparently, is not the only one. It is known that certain explosives, for example picrates of metals, also possess a very high burning rate and nonetheless do not refer to the class of initiating explosives. On the other hand, such typical initiating explosives, such as lead azide, in general do not burn and upon igniting immediately, without which there would be no period of burning, they detonate.

Due to the significant combustion instability of initiating explosives, it is quite difficult to study this process and the causes of its transition into an explosion. Meanwhile, it is known that certain mixtures of initiating explosives with inert substances, and also secondary explosives are capable of burning completely stably. Thus, mixtures of lead azide with gelatin nitroglycerine and nitrocellulose [2], [3], [5] burn stably at atmospheric pressure even with contents in them of up to 30—40% azide.

It is interesting to explain the influence of pressure on the character and burning rate of similar mixtures with different contents of azide and near

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the area of conditions, leading to transition of burning into explosion. As secondary explosives were applied liquid nitro esters (nitroglycol, nitroglycerine and diglycoldinitrate), usually gelatinized by a small quantity of collodion. Of the initiating explosives, besides lead azide, lead styphnate and potassium picrate were also partially studied.

Methodology of Conducting the Experiments

Liquid nitro esters were gelatinized by a small quantity (3%) of collodion (12% N) and carefully mixed with an initiating explosive, sifted through a silk sieve with 39 apertures per centimeter. Mixing was done with a wooden stick in a well glazed porcelain cup. The obtained mixture was sucked or stuffed into tubes of molybdenum glass with fused ends. The diameter of the tube usually constituted ~5 mm, the height of the charge 1--2 cm. Determination of the density of charges of one of the mixtures prepared in this manner showed that this density is near to the theoretical one.

At increased (to 70 at) pressures the experiments were conducted in cylinders to study the burning of explosives at constant pressure. Experiments in this cylinder were conducted in an atmosphere of nitrogen, rarer -- carbon dioxide. Igniting was done with an incandescent current of Nichrome wire through a layer of gelatinized nitroglycol or directly. Speed and character of burning was fixed with the help of photoregister, and in a number of cases -- AK-16 a movie camera.

Results of Experiments

Mixtures of Lead Azide With Nitroglycol

Upon igniting a mixture of slightly gelatinized nitroglycol with 10% lead azide in air in tubes 5 mm in diameter after combustion of a layer approximately 2 mm thick attenuation occurs. In tubes 7 mm in diameter a layer 3--4 mm thick burns, and at a diameter of 10.5 mm--a layer 4--5 mm. Burning is accompanied by strong frequent crackling, and sometimes from the tube pieces of the mixture nearly a millimeter in size fly out.

Increase of pressure stabilizes burning easier, the larger the diameter of the tube. At a diameter of 5 mm the mixture died out at 4 and 5 at and started to burn only at 6 at. At a diameter of the tube of 7 mm burning occurred at 4 at. At higher pressures the mixture burns stably with a speed practically equal to the burning rate of pure gelatin (Fig. 1). The secondary flame of the mixture, clearly noticeable in the photographs, starting from a pressure of 8 at, is not dull red, as in burning of one gelatinized nitroglycol, but bright white. The width of the dark zone between it and the surface of the condensed phase is near to the width of this zone in the case of burning gelatinized nitroglycol (Fig. 2). At a pressure of approximately 20 at in certain photographs (Fig. 3) 4 wave zones of burning are visible.

With large concentrations of azide in the mixture, igniting it leads not only to attenuation, but also to explosion of the charge. From Fig. 8, located in article 27 (see page 608 of the collection) and depicting the influence of composition, pressure and method of ignition on the behavior of mixtures of lead azide with gelatinized nitroglycol, it is clear that, by increasing the pressure, it is possible to prevent attenuation or explosion and to obtain stable burning of the mixture. The appearance of an explosion is facilitated by igniting the mixture directly with a heated wire, especially if it is introduced to the substance at a certain depth. It is completely natural that with large contents of azide an explosion occurs easier than with small. With contents in the mixtures of 75% PbN_6 stable burning of it is not stimulated even with an increase of pressure to 54 at.

The pressure, beginning from which the mixture becomes capable of stable

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burning, with an increase of contents of aside in it, considerably grows. This growth is expressed by the relationship

$$P_{cr} = 4.10e^{1.32m}, \text{ kg/cm}^2 \text{ (see Fig. 4)},$$

where m is the contents of lead aside in mixtures with gelatinized nitroglycol in g/cm^2.

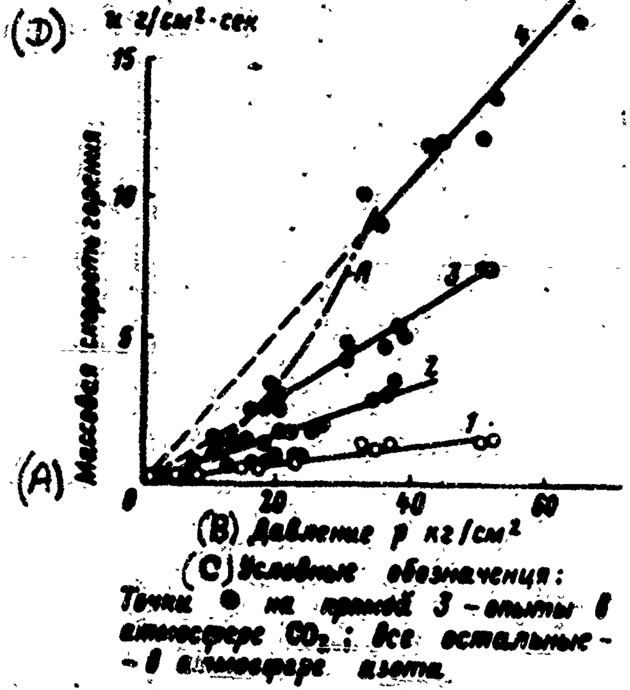

Fig. 1. Influence of pressure on burning rate of mixtures of lead aside with gelatinized nitroglycol.
Percentage of PbN_6 in the mixtures: 1 --○ -- ⊘; ● -- 10; 2 -- 30; 3 -- 50, 4 -- 60; dotted line A separates the area of stable burning from the area in which the mixtures die out or explode.
A) Mass burning rate; B) Pressure p kg/cm^2; C) Conditional designations: Points o on straight line 3 - experiments in an atmosphere of CO_2; All remaining - in an atmosphere of nitrogen; D) u $g/cm^2 \cdot sec$.

The burning rate of similar mixtures (see Fig. 1) is approximately proportional to pressure. The dependence of the proportionality factor (B) on composition of the mixture can be presented in the form of

$$B = 0.035e^{1.31m} \text{ g/cm}^2 \text{ sec: kg/cm}^2 \text{ (see Fig. 4)}.$$

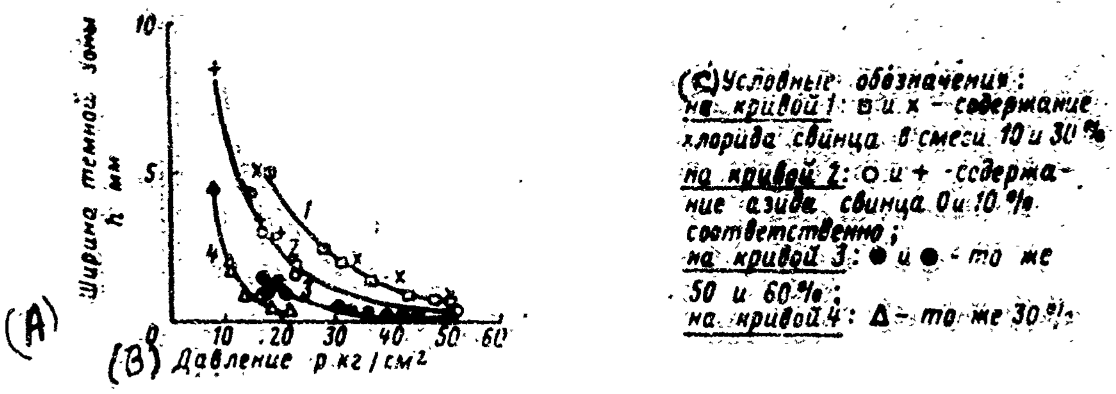

Fig. 2. Influence of pressure on width of dark zone during burning of mixtures of lead azide and chloride with gelatinized nitroglycol. 1--mixtures with $PbCI_2$, 2, 3, 4--mixtures with PbN_6. (30% mixture of lead azide is insufficiently uniform and burns nonuniformly) A) Width of dark zone; B) Pressure p kg/cm²; C) Conditional designations: on curve 1: ▫ u x – contents of lead chloride in mixtures of 10 and 30%; on curve 2: o u + – contents of lead azide of 0 and 10% correspondingly; on curve 3: ● u ● – the same 50 and 60%; on curve 4: Δ – the same 30%.

In Fig. 5 are photographs of burning of mixtures of lead azide and gelatinized nitroglycol with a content of 30, 50 and 60% PbN_6. The flame during burning of these mixtures usually consists of three zones, and the width of the dark zone is less than during burning of gelatinized nitroglycol (Fig. 2).

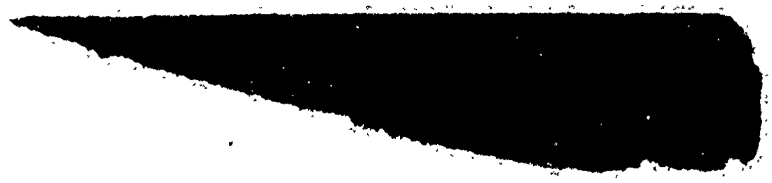

Fig. 3. Burning of a mixture of lead azide with gelatinized nitroglycol 10:90 at a pressure of 22 at (negative).

For preparation of a mixture with 30% PbN_6, as distinguished from other mixtures azide was used, not passed through a sieve and containing together with the thinly-dispersed substance small lumps of adhering powder. This mixture especially easy exploded at low pressures, and at increased — burning of it, although it was fully stable, occurred extremely nonuniform (Fig. 5, d).

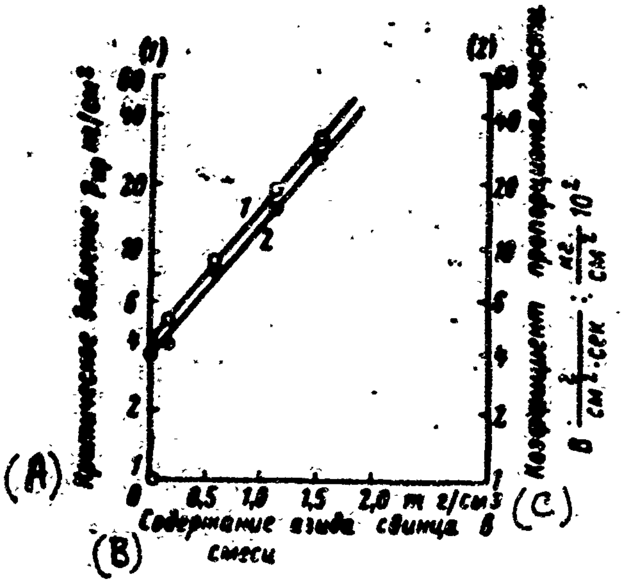

Fig. 4. Dependence of burning rate and critical pressure on composition for mixtures of lead azide with gelatinized nitroglycol. 1—critical pressure, 2—proportionality factor B in the equation u_m = Time. A) Critical pressure p_{cr} kg/cm^2; B) Contents of lead azide in mixtures; C) Proportionality factor, $B\ \frac{g}{cm^2 \cdot sec} : \frac{kg}{cm^2}\ 10^2$.

Mixtures of Lead Azide With Nitroglycerine and Diglycoldinitrate

Mixtures of lead azide with other liquid nitro esters behave analogous to mixtures of it with gelatinized nitroglycol.

Thus, a mixture of equal quantities of azide and slightly gelatinized nitroglycerine at 2 at died out, but already starting with 3 at and higher stable burned with a speed, approximately linear increasing with pressure (Fig. 6).

A mixture of 50:50 lead azide with nongelatinized nitroglycerine behaved analogously. Upon igniting it at 3.7 at an incomplete explosion occurred at 4.9 at the mixture died out, at 5.4 at — it ignited and smoothly burned. At a distance of nearly one centimeter above the surface of the condensed phase a yellowish secondary flame was observed. At higher pressures the mixture is well ignited and stably burns with a speed, somewhat greater (Fig. 6), than the burning rate of a gelatinized mixture, but significantly (approximately twice) as less, than the burning rate of nitroglycerine without lead azide [6]. Only in one experiment (at 33 at) at the end of burning a weak explosion was observed.

A mixture on the basis of gelatinized diglycoldinitrate 50:50 at moderately increased pressures (38 and 47 at) did not burn or, burned a little and died out (51 at); at 53, 55 and 60 at stable burning was observed with a speed 1--1.5 cm/sec.

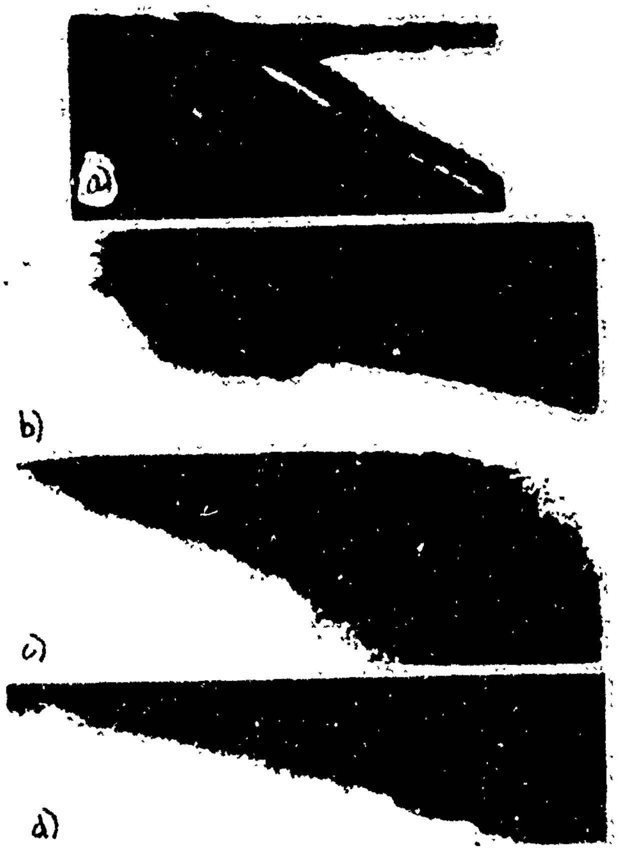

Fig. 5. Burning of mixture of lead azide with gelatinized nitroglycol. Percentage of PbN_6 in mixtures and pressure. a--50% and 21 at (positive), b--60% and 32 at (negative, at the end of burning is an explosion, well seen is the transition from burning of a layer of gelatinized nitroglycol to burning of the mixture), c--60% and 65 at (negative), d--30% and 25 at (negative, burning is stable but non-uniform).

On the photographs, a bright narrow strip of flame is noticeable near the surface of the condensed phase (Fig. 7); burning is accompanied by a set of weak flashes, adding a characteristic striped form to the photograph.

Fig. 6. Dependence of burning rate of mixtures of lead azide with nitroglycerine 50:50 on pressure. 1--nitroglycerine, nongelatinized, 2--nitroglycerine, gelatinized. a - u cm/sec.; b - p kg/cm^2.

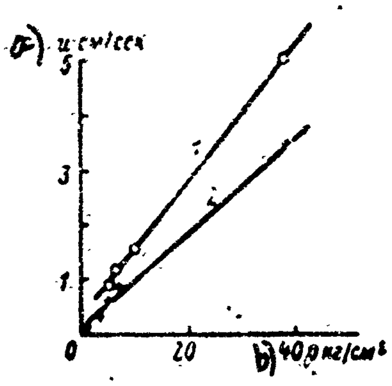

Fig. 7. Burning of a mixture of lead azide with gelatinized diglycoldinitrate 50:50 at a pressure of 60 at (negative).

Mixtures of Lead Styphnate With Nitroglycol

A mixture of 30% lead trinitroresorcinate (TNRL) with gelatinized nitroglycol at atmospheric pressure in tubes 5 and 7.5 mm in diameter dies out. At a diameter of 10.5 the mm mixture slowly burned with frequent strong crackling. At increased pressure the mixture burns evenly and stably with a speed, near to the burning rate of a mixture of nitroglycol with 30% lead azide (Fig. 8 and 9).

At an increase of contents of TNRL to 50%, the burning rate and pressure, starting from which the mixture burns stably, are increased, and distribution of the flame becomes nonuniform (see Fig. 10 and 11).

A mixture, containing 60% TNRL, at atmospheric pressure gives an explosion (upon igniting both directly by a heated wire, and also through a layer of gelatinized nitroglycol).

Fig. 8. Burning of a mixture of 30% TNRL with gelatinized nitroglycol at a pressure of 20 at (negative).

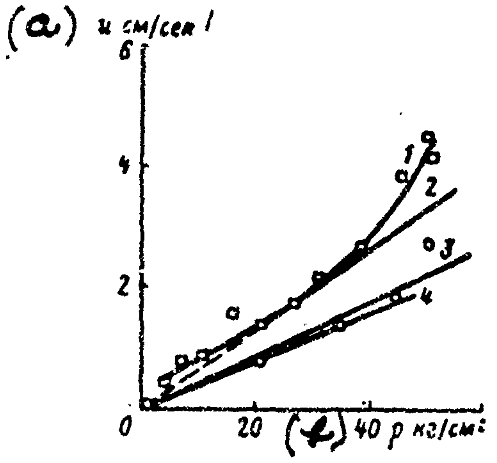

Fig. 9. Influence of pressure on burning rate of mixtures of lead styphnate and azide with gelatinized nitroglycol. 1 and 4—mixtures with TNRL 50 and 30%. 2 and 3—mixtures with PbN_6 —50 and 30% (correspondingly). a) u cm/sec; b) p kg/cm^2.

At increased pressures the mixture burns, although extremely nonuniform, but without transition to explosion, and besides the burn-up time of the charge by measure of increase of pressure is increased, i.e. the average speed of burning is decreased (see Fig. 11).

Mixtures of Potassium Picrate With Diglycoldinitrate and Nitroglycol

The influence of composition on burning of a mixture of potassium picrate with gelatinized diglycoldinitrate at atmospheric pressure in tube 11 mm in diameter is illustrated in Fig. 12[1]. A mixture, containing nearly 5% picrate, burns with sonorous crackling and with a speed, near to the burning rate of pure gelatin.

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[1] These experiments were conducted by the student V. I. Kozlov.

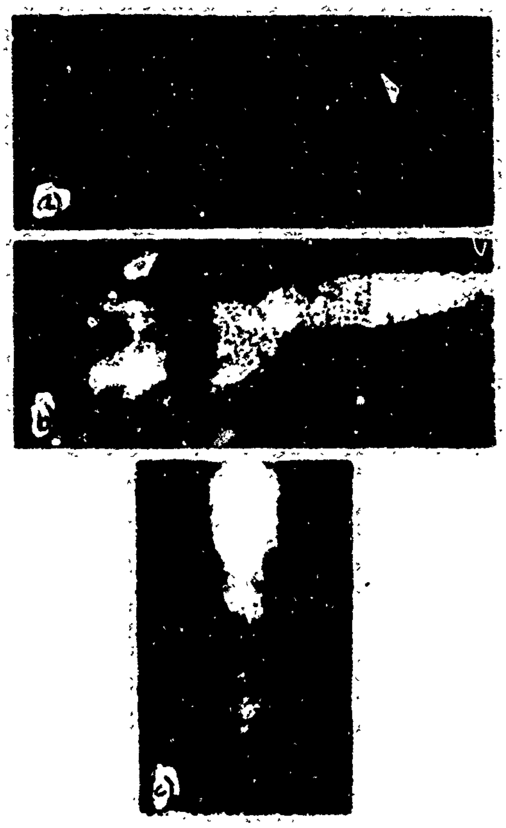

Fig. 10. Burning of a mixture of 50% TNRL with gelatinized nitroglycol under pressure: a—7, b—51, c—37 at (positive).

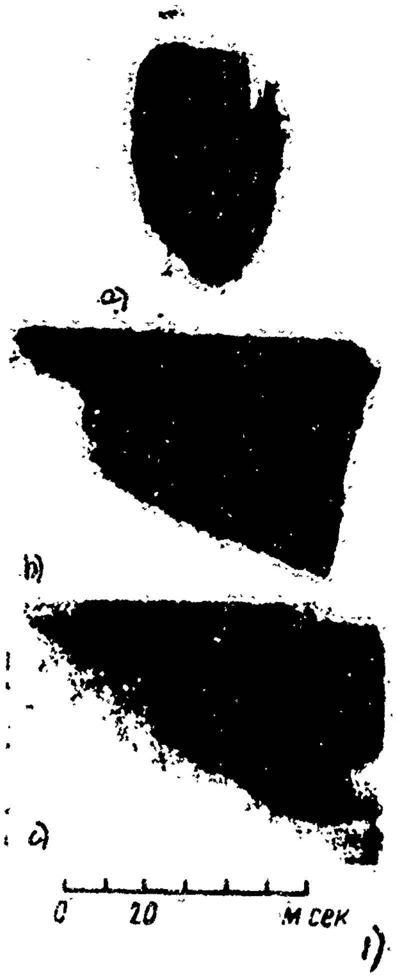

Fig. 11. Burning of a mixture of 60% TNRL with gelatinized nitroglycol under pressure: a—37, b—51, c—62 at (negative). 1) M sec.

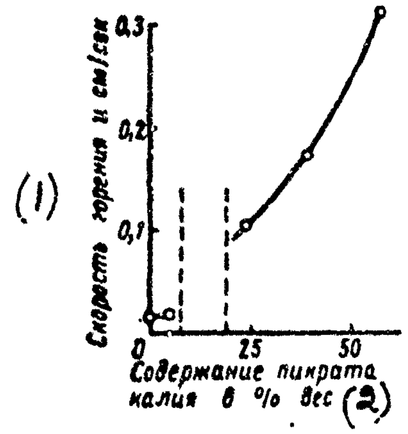

Fig. 12. Dependence of burning rate of a mixture of potassium picrate with gelatinized diglycoldinitrate at atmospheric pressure on composition. 1) Burning rate, u cm/sec; 2) Contents of potassium picrate in % by weight.

Mixtures with 8.9 and 19% picrate do not burn, and starting with 24% again become capable of burning, and the speed of the latter is several times higher than pure diglycoldinitrate. At an increase of contents of picrate in the mixture, the crackling, accompanying the burning, is increased and at 50--70 % changes into even strong hissing. Mixtures of potassium picrate with gelatinized nitroglycol behave analogously, but burned faster and at an increase of the contents of picrate burning of them was stopped later, than the diglycoldinitrate mixtures.

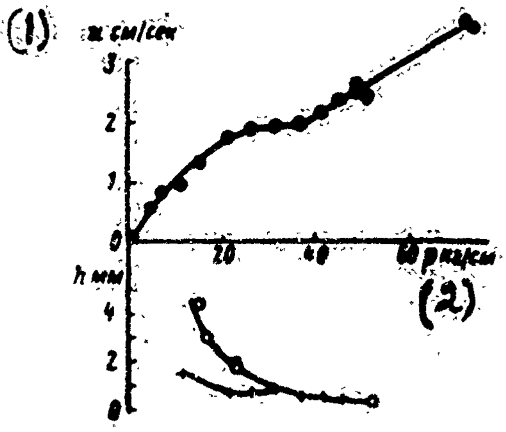

Fig. 13. Influence of pressure on burning rate (u) and width of dark zone (h) during burning of a mixture of equal quantities of potassium picrate and gelatinized nitroglycol. + — width of dark zone during burning of mixture, 0 — width of dark zone during burning of gelatinized nitroglycol without addition of picrate. 1) u cm/sec.; 2) p kg/cm^2.

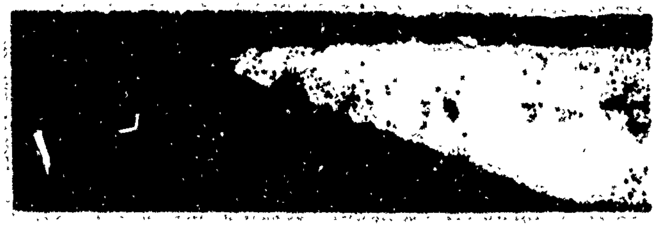

Fig. 14. Burning of a mixture of potassium picrate with gelatinized nitroglycol during igniting through a layer of gelatinized nitroglycol, pressure 31 at (positive).

The dependence of the burning rate of a mixture of equal quantities of potassium picrate and gelatinized nitroglycol on pressure is presented in Fig. 13. Upon igniting through a layer of gelatinized nitroglycol this mixture in the range of 1--75 at burns stably and evenly. In a wave of burning it three zones are noticeable (Fig. 14), and both the primary and secondary flames are dimmer, than in the case of mixtures, containing lead salt.

Fig. 15. Nonuniform burning of a mixture of potassium picrate with gelatinized nitroglycol during igniting directly by a heated wire, pressure 20 at (positive).

The dependence of the width of the dark zone on pressure is quite original (Fig. 13): at moderately increased pressures this zone is already significant, than during burning of pure gelatin, and at higher pressures this distinction disappears.

In the case, when the mixture was ignited directly by wire, burning was nonuniform, unstable and its speed according to photographs, obtained on a photoregister (Fig. 15) was not able to be determined.

Mixtures Containing Lead Chloride

An increase of the burning rate, change of critical diameter, decrease of thickness of the dark zone and other effects, observed with the addition to nitro esters of lead azide and TNRL, would have been possible to add to the catalytical influence of the lead contained in them. In order to establish the possible role of this factor, we conducted experiments on burning of mixtures of gelatinized nitroglycol with chloride of bivalent lead. It turned out that an addition of 10 and 30% $PbCl_2$ almost does not have an influence on the burning rate of nitroglycol (Fig. 16) and, consequently, somewhat increases the mass speed. It is obviously, however, that this effect does not compare with the action of lead azide and TNRL on the burning rate and, consequently, the role of catalysis in the increase of the burning rate of nitro esters upon addition to them of quick-burning compounds of lead is small. The flame, during burning of mixtures containing lead chloride, has a complicated polyzonal structure, and in certain photographs it is possible to distinguish up to five zones (Fig. 17). The width of the first dark zone somewhat exceeds the width of it during burning of gelatinized nitroglycol and all the more so -- high-percentage mixtures of it with lead azide (see Fig. 2) which also indicates the distinction in mechanisms of action of these substances.

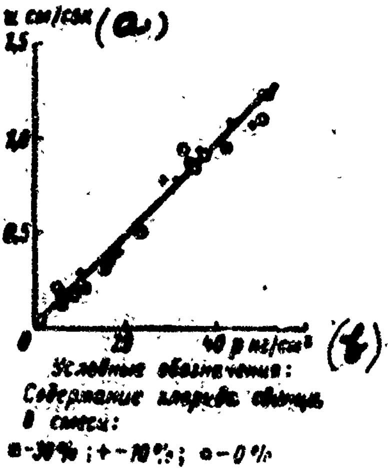

Fig. 16. Influence of pressure on burning rate of mixtures of gelatinized nitroglycol with lead chloride. 1) Conditional designations: Contents of lead chloride in mixtures: ▫ - 30%; + - 10%; o - 0%. a) u cm/sec.; b) p kg/cm².

Fig. 17. Burning of a mixture of 30% $PbCl_2$ with gelatinized nitroglycol at a pressure of 50 at (negative).

Discussion of Results

The main result of the above described experiments consists in revealing the original influence of pressure on the possibility of burning of mixtures of initiating explosives with liquid nitro esters. Unstable at atmospheric or moderately increased pressure, the burning of these mixtures, as a rule, is completely stable at high pressures. This effect is exhibited for mixtures of nitro esters both with lead azide, and also with lead styphnate. The paradoxicalness of it is specially graphic in those cases, when an increase of pressure prevents not only attenuation, but also explosion of mixtures (see for example the data for a mixture of gelatinized nitroglycol with 30% PbN_6 in Fig. 8, Article 27, page 608). The originality of such an influence of pressure is exhibited even in the fact that a mixture of 50:50 lead azide with nitroglycerine, the capability of which for normal (undisturbed) burning is much less than nitroglycol, burns, starting from lower pressures, than a nitroglycol mixture. In the first case burning starts with 3 at, in the second — only with 20 at.

It is completely obvious that to explain these phenomena, proceeding from usual presentations about the mechanism of disturbance of burning and its transition into an explosion [1] would be difficult. Indeed, the usual presentations are based on numerous facts of the directly opposite influence of pressure on stability of burning of explosives and logically explain them by the fact that upon increase of pressure the burning rate and dynamic increase of pressure are increased. Upon achievement of a certain critical pressure, the heated gaseous products start to penetrate into the depth of the charge, the surface of burning is increased, its speed and dynamic increase of pressure progressively increase, burning becomes nonuniform, pulsating or changes into an explosion.

The original influence of pressure on the stability of burning of explosives observed in our experiments can be, however, naturally explained, if we proceed from the presentation [2], [3] about the fact that transition of burning into explosion is combined with the coverage of the chemical reaction of a layer of the explosive of a certain critical thickness. Explosion of this layer, more accurately, suspensions of explosive particles, formed during the reaction in it, if it leads to formation of a sufficiently large jump in pressure, causes an explosion of the remaining part of the charge. If the jump in pressure is insufficient, then attenuation occurs, due to disturbance of the heated layer, or at small amplitude of this jump the burning acquires a pulsating character. The appearance of an explosion of the suspension depends also on the time of stay of the initiating explosive in the heated state. If this time is less than the period of induction, then a layer of the mixture burns earlier, than the initiating explosive flashes.

The fact that pressure is not directly important, and namely the thickness of the heated and reacting layer and duration of its existence, is indicated by the dependence of the phenomenon on the burning rate of nitro esters. Mixtures on a base of nitroglycerine, burning faster than nitroglycol, acquire the ability to burn stably, starting from smaller pressures, slowly burning mixtures on a base of diglycoldinitrate, conversely, provide stable burning only at significantly larger pressures, than nitroglycol mixtures. The burning rate at pressures, starting from which mixtures of 50:50 on a base of nitroglycol and diglycoldinitrate burn stably (20 in the first and $\sim$50 at in the second case) are approximately equal and constitute nearly 1 cm/sec.

It is easy to explain also from this point of view the completely unusual phenomenon, observed upon addition of the least capable of burning initiating explosive — lead azide to one of the most easily exploded and difficulty burning secondary explosives — nongelatinized nitroglycerine. In that region of pressures, in which nitroglycerine due to turbulence of the liquid surface does not burn, and azide, as is peculiar to it, detonates, and a mixture of equal quantities of these substances is capable of stable burning. Above it was already noted that at those increased pressures, with which nitroglycerine again starts to burn, but even in turbulent conditions, i.e. with great speed, the addition to it of lead azide, obviously hampering turbulence, sharply (approximately twice) lowers the burning rate. The latter is observed also during burning of liquid nitroglycol with lead azide at pressures higher than 20 at.

If upon igniting, a thicker layer of mixture is heated, the probability of the appearance of an explosion in it, obviously, increases. This case is illustrated by experiments with a 30% mixture of lead azide with nitroglycol upon igniting with incandesced current through a wire (Fig. 8 Article 27, page 606). In that case, if the ability of the system to explode is less significant, than mixtures with lead azide, igniting by wire can lead not to explosion, but to nonuniform disturbed burning in those conditions, in which upon "softer" igniting the system burns evenly and smoothly. Thus behaves, for example, a mixture with potassium picrate (cf. Fig. 14 and 15).

A thermal explosion, leading to attenuation of a mixture, certainly should not envelope the whole heated layer. It was noted above that burning of the investigated mixtures at atmospheric pressure is accompanied by frequent crackling — obviously micro-flashes of particles of a quick-burning explosive or their aggregates. These micro-flashes, mixing the heated layer and reinforcing the heat supply, mix the distribution of burning and at a sufficient contents in the mixture of a quick-burning substance lead to attenuation. In that case, if a quick-burning explosive is capable of independent burning, at a significant contents of it in the mixture, the latter can begin to burn again, but already in conditions, peculiar to a pure quick-burning substance (at small contents of a quick-burning explosive, this, obviously, agitates the nitro esters, in particular by the fact that it absorbs heat in its own evaporation). Precisely in this manner, mixtures with potassium picrate behave and a mixture with nitroglycol dies out with a larger content of picrate, than with slowly burning diglycoldinitrate. The picture, apparently, similar to that described above, was observed by A. F. Belyayev [5] for mixtures of lead styphnate with trinitrotriazide benzene.

The obtained data allow also to estimate the burning rate of lead azide with larger approximation, than this it was possible to do on the basis of preceeding works. Substituting into the equation $u_m = 0.035\, e^{1.31m}\, p$ (g/cm^{2}sec) the value $m = 4.71$ g/cm^3 (specific gravity of lead a-azide), we will obtain a burning rate of pure lead azide at atmospheric pressure equal to $\sim$3.5 cm/sec.

Let us remember that according to Belyayev [5] the burning rate of lead azide is at least an order larger and constitutes 50--100 cm/sec. One should note, however that this magnitude is obtained by extrapolation on pure azide of the burning rates of mixtures of it with mercury fulminate at the temperature of liquid nitrogen. The contents of azide in the mixture did not exceed 15% (with this concentration, burning changed into detonation). It is obvious that the reliability of the magnitude, obtained so far by extrapolation, with such exotic fuel as mercury fulminate, the same as in a completely unknown area of low temperatures is very small.

Apparently, the speed, with which lead azide would burn, if it could burn at atmospheric pressure, is significantly lower. This is indicated, in addition, by the results of experiments on burning of mixtures of lead azide with mercury fulminate and with lead styphnate, conducted by B. S. Svetlov in 1952. During the study of burning of these mixtures (with addition of small quantities of bitumen) in a manometric cylinder it was shown that the introduction into a mixture of azide very greatly decreases the burning rate of styphnate and practically does not change this burning rate of mercury fulminate. On this basis it is natural to assume that the burning rate of lead azide is little distinguished from the burning rate of mercury fulminate (at atmospheric pressure $\sim$1.5 cm/sec [7]) and is significantly less than lead styphnate ($\sim$30 cm/sec) [8].

If this assumption is correct, then an explanation of the absence in lead azide of the ability of stable burning with a phenomenally great burning rate of this substance, obviously, is erroneous. Apparently, the considerations, which are concluded in the fact that an explosion of lead azide upon ignition is stipulated by intense dispersion and explosion-like combustion of a layer of the formed suspension [4], and are more well-grounded and better reflect the essence of the phenomenon.

The author is deeply thankful to professor K. K. Andreyev for his help in carrying out this work and the explanation of its results.

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IT-63-254

Chapter 3 Article 30

Pages 457 - 467

A. I. Gol'binder

30. Certain Regularities of Burning of Volatile Multicomponent Explosive Substances

In the burning of certain liquid explosive mixtures (ZhVS) we detected unique changes in the speed and character of burning with its propagation. In case of volatile explosives, which include the studied ZhVS, the mechanism of phenomenon called fractional burnout, consists briefly in the following.

In the process of burning, as is known [2], the initial stage can be evaporation of the explosive/ and/ chemical reactions, and, correspondingly, heat liberation, will proceed mainly, if not exclusively, in the gas phase in vapor. For such substances the thermokinetic characteristics of the leading reaction of burning, and consequently, also the rate and character of the latter, are determined not by the composition of the condensed explosive but by the composition of the vapor over it. During burning of individual explosives the composition of the vapor coincides with that of the condensed phase and in any case, remains constant during burning in constant conditions. On the other hand, when the explosive is a mixture of several components, whose vapor tension at an identical temperature are considerably different, the composition of the vapor can more or less significantly be distinguished from the composition of the liquid and can change by the measure of its evaporation (burnout). The change of composition of the vapor will lead to a change in the speed and character of burning. In definite conditions the compositions of the heated surface layer and the remaining liquid can be levelled sufficiently fast. In such cases we observe a more or less continuous change in the composition of the mixture and, correspondingly, the characteristics of its burning by the measure of the propagation of the latter. In other cases, when conditions for equalizing of concentrations are unfavorable, the corresponding changes in the compositions of the liquid and vapor steam, and consequently the burning rate, will occur only in the process of burnout of a comparatively thin heated layer. In such conditions fractional burnout can lead to periodic changes of characteristics of burning — pulsations of different frequency and amplitude.

Experimental Part

In a large part of the experiments described below ZhVS was burned in air at atmospheric pressure and room temperature in glass pipes with internal diameters about 0.5 cm. Ignition was produced by a wire spiral, incandesced by current.

Mixtures With Tetranitromethane

In these conditions a stoichiometric mixture of benzene and tetranitromethan (content of benzene 13.7% by weight) at first burns at a very low rate — about 0.01 cm/sec. The surface of the burning liquid remains during this time complete even, the flame front adjoining it gleams extraordinarily weakly and above the cut of the pipe a secondary flame is observed. Below we will call such a regime burni with a small speed.

By the measure of combustion the burning rate grows at first slowly and then faster. Original height of the column of ZhVS in pipe constituted in our experiments 5—10 cm. After 40—45% original quantity of mixture is burned, the burning r is increased comparatively quickly (on the 3—5 mm section) by 2—3 times and will attain 0.05—0.06 cm/sec. With this speed the character of burning clearly change a bright flame appears above the meniscus of the ZhVS, in the surface layer of th burning liquid separation of numerous small bubbles is observed, the secondary flame disappears. In such a regime, called in the future burning with great spee the process goes to completion.

By the measure of the increase in the content of oxidiser in the mixture of tetranitromethane and benzene the mean value of small speed[1] is increased, but the length of the section on which this regime of burning exists is reduced. With a content tetranitromethane in the mixture of 90% by weight and more, burning proceeds with great speed from the moment of ignition.

By the measure of the increase in the content of benzene in the original mixture, in the area negative oxygen balance. A decrease is observed in the mean value of the small speed and the length of the section on which burning proceeds in this regime increases. Finally, at a content of benzene of more than 20% by weight, burning in the given conditions of experiments (diameter of pipe, temperature) becomes impossible. Results of experiments with mixtures of various original composition are presented in Fig. 1, where besides values of small and great burning rates there are drawn also the equilibrium curves of the beginning of boiling and condensation of the ZhVS, calculated by the vapor tension of the pure components on the assumption that the mixture is ideal. Besides, on graph are drawn also experimental points "beginning of boiling"[2].

We noted above that once the regime of great speed is established, burning with this regime method goes to the end. The burning rate, however, does not remain constant, but decreases very slowly. A gradual decrease in the great speed is observed both during the burning of mixtures of an original composition with which on the initial section the process goes at small speed, and with mixtures with a positive oxygen balance, where there is no such section. During the burning of a layer of

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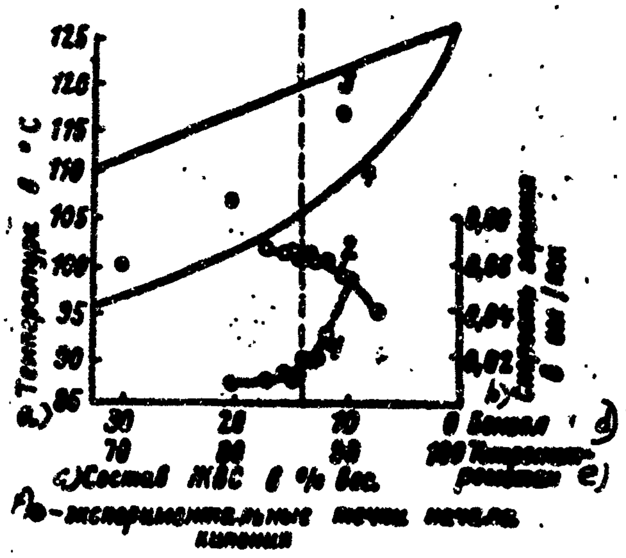
[1] Here and in the majority of subsequent experiments burning rate is determined as the ratio of the length of a certain section of the liquid column (usually no less than 1 cm) to the time of its combustion, measured by a stop watch.

[2] In connection with evident difficulties of equilibrium analysis of "liquid--vapor" for highly sensitive ZhVS, we were limited by determination of the temperatures of beginning of boiling by the method of M. N. Sivolobov [7]. Control experiments with well-studied nonexplosive binary systems showed that the determination by such a method of the temperature of beginning of boiling gives a result 3—7° higher than equilibrium temperatures.

ZhVS with an initial height of 6.5 cm, we measured the burn-up time three sections 2cm in length. For a mixture of 10% benzene and 90% tetranitromethane the average speed of burning on the upper section of the measurement constituted 0.06 cm/sec, and on the lower section — 0.05 cm/sec. For a mixture containing 7% by weight benzene in analogous conditions the corresponding speeds were 0.050 and 0.035 cm/sec.



Dotted line marks stoichiometric composition.

Fig. 1. Dependence of average speed of burning of a mixture tetranitro methane and benzene on composition.

1—average speed of propagation of flame on section of burning with small speed; 2—average speed of propagation of flame on section of burning with great speed; 3 and 4—equilibrium curves of condensation and boiling points. a) Temperature, °C; b) Burning rate, cm/sec; c) Composition of ZhVS, % weight; d) benzene; e) Tetranitromethane; f) experimental points of beginning of boiling.

With a growth in initial pressure the burning rate of the considered ZhVS, as for other volatile explosives, increases. With this the changes in the speed and character of burning with burnout weaken and, starting from a pressure of about 1.5 kg/cm^2, become inappreciable; the front of burning is spread with visible uniformity along the entire length of the pipe[1].

Changes in the speed and character of burning with the measure of burnout, more or less similar to those described above, were observed during the burning of certain other binary ZhVS of tetranitromethane with liquid fuels, for example, wit

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[1] With an increase of initial pressure higher than 2 kg/cm^2, burning changes to a turbulent regime, and with still higher pressure transition of burning to detonation is observed. These phenomena we will not examine here.

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methanol, ethanol ethyl nitrate, diethyl ester, toluene, etc. From the number of studied ZhVS, we will list data for a mixture with ethyl-nitrate, where these changes are sharpest and most unique. If we determine the dependence "average speed of burning — composition of ZhVS", then for mixtures of tetranitromethane with ethyl-nitrate it is possible to note in a definite interval of concentrations a sharp maximum of speed. Mean speeds, calculated by the time of combustion of a layer of mixture about 5 cm in height, are presented in Fig. 2. In the interval of nitrate concentrations from 28 to 35% the burning rate sharply increases; almost immediately after ignition, burning changes to a turbulent regime, and in two cases (marked in Fig. 2 by arrows) explosion was triggered. During fast burning, phenomena of fractional burnout are absent. Burning of mixtures whose initial composition lies outside the indicated interval of concentrations proceeds with a speed which varies strongly during propagation. A series of mixtures of tetranitromethane and ethyl nitrate of different initial composition were burned in pipes 6—8 cm in length and burn-up time was measured on different sections of layer of liquid.

The results of the experiments presented in Fig. 3. The burning rate, calculated by the time of combustion of definite sections along the length of charge, was carried during construction of graph to the middle parts of the corresponding sections. Each of the curves in Fig. 3 was constructed from 2 — 4 parallel experiments. From the graph of Fig. 3 it is clear that burning of mixtures containing a significant (vs. stoichiometric) surplus of fuel is accelerated during the propagation of the process. On the other hand, the burning rate of mixtures with a large surplus of oxidizer decreases with combustion, is sometimes so significantly that burning dies out.

During the burning of many mixtures of tetranitromethane with liquid organic fuels, no systematic changes in the speed of propagation of the flame were observed and burning proceeded with clear (during visual observation) uniformity. Such ZhVS include, for example, solutions in tetranitromethane of octanol, nitrobenzene, diglycoldinitrate, mononitrobenzene, mono- and dinitrotoluene, etc.

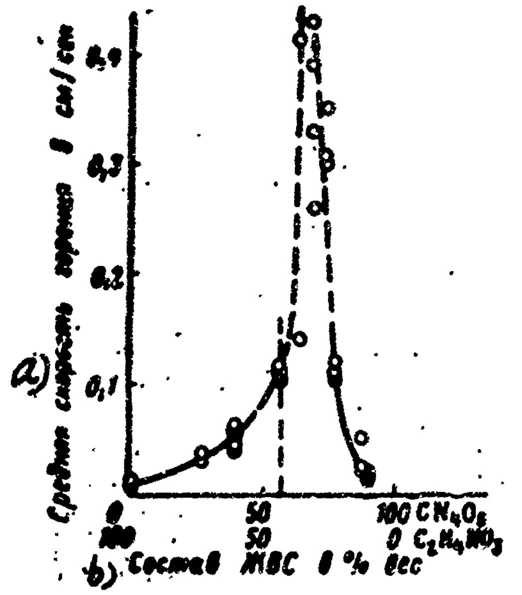

Fig. 2. Dependence on composition of average speed of burning of a mixture of ethyl-nitrate and tetranitromethane.

a) Average speed of burning in cm/sec;
b) Composition of ZhVS in wt %.

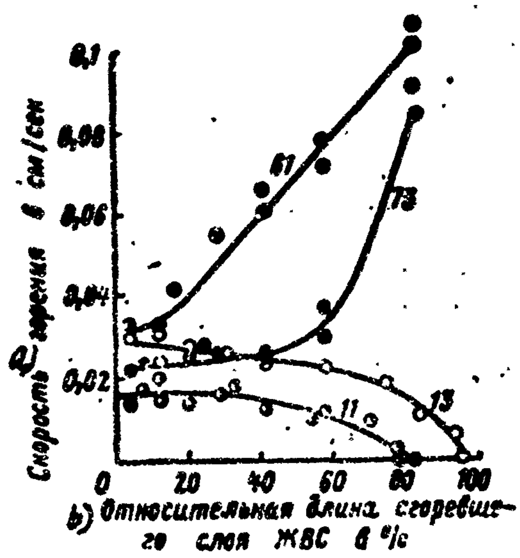

Fig. 3. Change of burning rate with burnout of mixtures of ethyl-nitrate and tetranitromethane of various initial compositions. (Numbers by curves —contents of ethyl-nitrate in original mixture in wt %).

a) Burning rate in cm/sec; b) relative length of burning layer of ZhVS in %.

Without listing all the experimental data on each of the studied ZhVS, we will enumerate below only the main general regularities detected in the course of the investigation:

1. In mixtures which vapor tension and composition deviate considerably[1] from the corresponding parameters of ideal systems, — we did not observe phenomena of fractional burnout, as a rule. Liquid — vapor equilibrium for ZhVS of tetranitromethane with organic fuels , so far as we know, has not been studied. In connection with this, there are not sufficiently reliable data on the nature and character of deflections from the ideal for various mixtures. In certain cases—for example, a mixture tetranitromethane with furfurole — a chemical compound will be formed;

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[1] As the index and standard of such deflection is we took the difference between temperature of beginning of boiling determined experimentally (see footnote 2 on page 647) and that found by calculations carried out by the laws of ideal mixtures.

in others, the formation of azeotropes is possible.

2. The phenomenon of fractional burnout of such character as was described above, for mixtures of benzene or ethyl nitrate with tetranitromethane were observed only in systems, where the component possessing large vapor pressure had simultaneously a density considerably smaller than that of the second component of the ZhVS. Thus the burning rate changed with propagation of the process for mixtures with methanol and ethanol, which have larger vapor pressures and smaller densities than tetranitromethane, but for the system octanol—tetranitromethane, where the oxidizer, possessing high density, is a more volatile component, such changes were not observed.

3. If we compare the properties of binary ZhVS of tetranitromethane with several fuels near each other in chemical nature, for example, with homologues, then it is possible to see that fractional burnout is observed the more clearly, the greater is the difference in the vapor tension and density of the components of the mixture. Thus the change in burning rate with its propagation is very significant for ZhVS with benzene and almost inappreciable for mixtures with toluene; analogous relationships can be noted for the series methanol—ethanol—propanol—butanol and others.

Mixtures With Nitric Acid and Nitrogen Tetroxide

Fractional burnout is characteristic for many ZhVS not only with tetranitromethane, but also with other volatile oxidizers. Let us consider, for example, data received for mixtures of nitrogen tetroxide and nitrobenzene. At atmospheric pressure and room temperature in pipes about 1 cm in diameter, mixture of the indicated components with a zero (content of nitrogen tetroxide 71.8 wt.%) and, all the more so, a positive oxygen balance — cannot burn. Mixture with a significant (vs. stoichiometry) surplus of fuel (content of nitrobenzene 36 wt % and more) burn in the given conditions. Burning is propagated at a low, gradually reduced speed (in the initial section about 0.01 cm/sec) and dies out after the burnout of a certain fraction of the mixture; this fraction is somewhat increased with a growth in the content of nitrobenzene in the original mixture.

Similar phenomena were observed during the burning of ZhVS based on concentrated (93—98%) nitric acid. A mixture of this oxidizer with mononitrobenzene at atmospheric pressure is capable of burning only in a definite interval of compositions. With this, after burnout of a certain part of the mixture, the burning rate is decreased so much that further propagation of the process in pipes of small diameter becomes impossible. The average speed of burning and the length of the burning layer of ZhVS grow with an increase in the content of fuel. The results of certain experiments conducted in glass pipes 9 mm in diameter at a temperature of 50° are presented in the table. At increased temperatures the burning rate of the given ZhVS, as well as of other explosives, is increased and simultaneously, the relative length of the layer of ZhVS burning to attenuation grows with an increase in temperature.

Table

Length of Layer of ZhVS of Concentrated Nitric Acid and Mononitrobenzene Burning at Atmospheric Pressure

(Initial Height of Layer 60 mm, Initial Temperature 50°, Internal Diameter of Pipe 9 mm)

1) Содержание горючего в смеси % объемн.	2) Длина сгоревшего слоя в мм		5) Примечание
	3) максимальная	4) средняя из 3—5 опытов	
27	0,5	—	—
29	4	2	—
31	10	7	6) Состав нулевого кислородного баланса
33	37	15	—
35	40	30	—

1) Content of fuel in mixture, vol %; 2) Length of burning layer in mm; 3) Maximum; 4) Average of 3 — 5 experiments; 5) Notes; 6) Composition of zero oxygen balance.

A significant number of experiments were carried out with mixtures of nitric acid and dichlorethane. Here also in many cases we observed attenuation after burnout of part of the mixture, and besides with a change in the relationship between components it is possible to note the following: mixtures with negative oxygen balance burn at a very small speed and die out quickly. The initial burning rate and length of burning of a layer of ZhVS increase with the increase in oxidiser. Maxima of the burning rate and the length of the burning layer are observed for mixtures with an approximately double surplus of acid vs. stoichiometry: a further increase in its content leads to lowering of the initial burning rate and reduction of the length of burning the layer. In Fig. 4 on the sections of the triangular diagram the results are shown of experiments on the burning of trinary mixtures of dichlorethane—nitric acid—water in glass pipes 5—7 mm in diameter at atmospheric pressure and a temperature of 40°. In these experiments we conditionally considered that the mixture is incapable of burning if the latter dies out before a layer 5 mm thick will burn. From the graph it is clear that the region thus defined of compositions promoting burning, is located asymmetrically relative to the line connecting compositions of zero oxygen balance. Mixtures containing a great surplus of oxidiser still promote burning with significant dilution by an inert component (water). In subsequent experiments we added to ZhVS, which by composition lay on limit of combustibility for given conditions, different quantities of oleum (about 20% free SO_3). It appeared that further dilution of liquid by inert substance makes it anew capable of burning. In experiments with mixtures containing oleum, a layer of more than 5 mm burned for all studied compositions up to that content of oleum at which stratification of the mixture starts. The tentative boundary of the region where dichlorethane, nitric acid, water, and sulfuric acid still will form single-phase systems is also shown in Fig. 4; all the tested mixtures, being inside this region, appeared capable of burning. In experiments with mixtures containing additions of oleum, burning never was propagated to the end of the pipe. Before attenuation we observed turbidity of the remainder of liquid, caused by the beginning of stratification into two liquid phases.

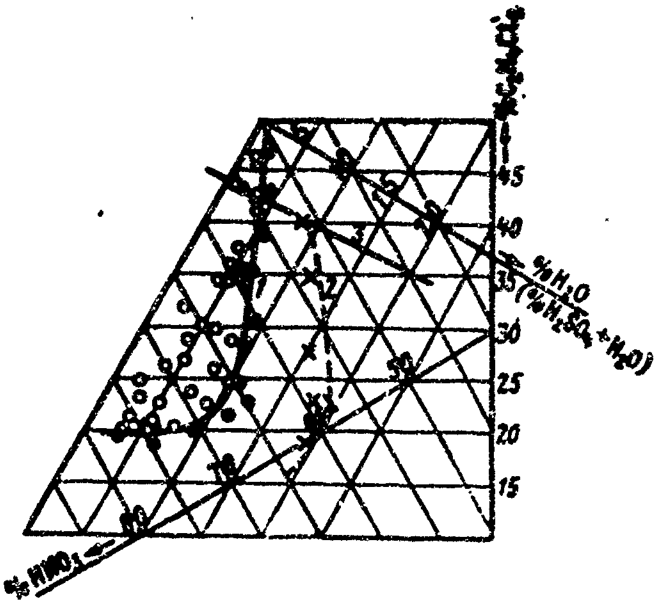

Fig. 4. Section of triangular diagram for mixtures dichlorethane—nitric acid—water.

0—burning propagated along a pipe more than 0.5 cm; X—the same, for mixtures with additions of oleum; ●—burning died out on a section less than 0.5 cm in length; 1—boundary of combustibility for trinary mixtures; 2—boundary of region of stratification of mixtures with additions of oleum; 3—line of stoichiometric compositions.

The change in the burning rate with burnout in a stoichiometric mixture of dichlorethane — nitric acid (97.3% HNO_3) can be seen by the results of experiments shown in Fig. 5. In these experiments, just as in those shown in Fig. 3, we measured burnup time of separate sections 0.5 cm in height along the length of the pipe, calculated the average speed of burning on a given section, and for construction of graph carried this speed to the middle of the corresponding section.

One should especially underline that fractional burnout, observed in certain of the studied ZhVS, occurred only at comparatively slow burning and at low pressure. With a growth in the pressure under which the burning proceeds, the changes in the speed of the latter by the measure of burnout of the ZhVS become all the weaker, and, starting from a certain pressure, are observed no more. For various ZhVS this pressure is different; in experiments with compositions near to stoichiometric, it constituted about 1.5 kg/cm^2 for a mixture tetranitromethane and benzene, about 5 kg/cm^2 for a mixture of nitric acid and dichlorethane, and more than 10 kg/cm^2 for a mixture of nitric acid and nitrobenzene.

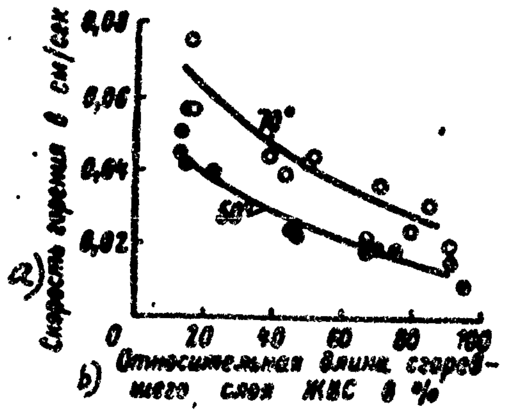

Fig. 5. Change in the burning rate in the course of burnout of mixture of dichlorethane and nitric acid at various temperatures.

a) Burning rate in cm/sec; b) Relative length of burning layer of ZhVS in %.

Solutions of Polymer in Liquid Explosives

The phenomenon of fractional burnout was observed not only for ZhVS of the type fuel—oxidizer. In work carried out jointly with V. V. Goryachev [4], is described the change in the speed and character of burning by the measure of its propagation for liquid explosives slightly thickened by the dissolution of high-molecular compounds (polymethylmethacrylate).

In the case of slowly burning ethylnitrate these changes are of the same character as for certain of the ZhVS described above: burning rate of the thickened nitro ester is decreased during propagation of the process up to a limit, at which burning in pipes of given diameter becomes impossible, owing to thermal losses.

In the case of quick-burning methylnitrate, the dissolution the smallest quantities of polymer abruptly changes the character of burning—it becomes pulsating, with short periods of relatively slow propagation alternated with more or less intense flashes. A noticeable fraction of the explosive burns quickly, precisely as a result of such flashes; this leads to a decrease in the general time of combustion of a column of the explosive of a given height, i. e., as if to growth in the burning rate. With an increase in the content of polymer in the solution, the frequency and intensity of pulsations increase. As was shown by high-speed filming, the burning of slightly thickened methylnitrate consists of a series of approximately identical cycles. At the beginning every cycle the surface of the burning liquid sinks slowly, remaining all the time level; the burning rate on this section is less than for unthickened methylnitrate(about 0.08 cm/sec at a polymer content of 0.1 wt. % and about 0.05 cm/sec at an addition in a quantity of 0.25%; unthickened liquid -- 0.12 cm/sec). Later bubbles appear in the surface layer of the liquid; a layer of foam will be formed, growing in thickness and, at last, there occurs sharp ejection of the surface layer into the zone of flame and its quick combustion in the form of a suspension of separate drops. After combustion of the suspension the cycle is repeated, the described pulsations like other manifestations of fractional burnout, are suppressed with the growth of initial pressure.

Discussion of Results

The study of the burning of mixtures especially graphically showed that it is the composition of the vapor and not of the actual liquid which determines possibility of burning in the given conditions, speed, and other characteristics of the process. Very characteristic in this respect are the results of experiments with mixtures of dichlorethane and nitric acid, given in the experimental section. Dilution of the mixture with water makes burning impossible, owing to the unfavorable composition of the vapor. With further dilution of the liquid with a ballast substance (oleum), burning becomes possible, since water is strongly bound to the monohydrate of sulphuric acid and does not proceed into the vapor phase in the beginning. In the case of a mixture of nitrobenzene and nitrogen tetroxide, the oxidizer has at identical temperature a significantly larger vapor pressure than the fuel. Therefore, if the composition of the liquid corresponds for example, to zero oxygen balance, the composition of the vapor over it contains a great surplus of oxidiser, with which burning under atmospheric pressure in a pipe of small diameter is impossible. Results of experiments with other mixtures can be explained analogously.

The decisive role of the composition of the vapor allows to explain also the observed phenomena of fractional burnout of ZhVS. Let us consider the somewhat detailed data on the burning of a mixture of tetranitromethane and benzene. Inasmuch as the vapor tension of benzene is noticeably higher than that of tetranitromethane, the concentration of fuel in the vapor should be considerably greater than in the liquid. By calculations carried out for an ideal mixture, at a content of benzene in the liquid of about 15 wt.% its content in the vapor will constitute more than 40%. As a result, over a liquid of stoichiometric composition the vapor will contain a significant surplus of fuel, which stipulates a very small initial burning rate.

In the process of burning the liquid is heated from surface; correspondingly from the surface there occurs evaporation; the surface layer of the ZhVS is impoverished of benzene and is enriched by tetranitromethane. Simultaneously there occurs equalizing of the composition of the surface layer and of all the remaining liquid, in the first place, with the help of gravitational currents, in connection with the fact that the density of tetranitromethane is almost twice that of benzene. With the enrichment by the oxidizer of the surface layer, its density becomes greater than that of the underlying layers of liquid, which favors mixing and equalizing of composition of liquid at significant depth from the surface. Equalizing of concentrations of different layers of liquid promotes also diffusion, but the speed of the latter in liquids is considerably less than that of convection mixing by the mechanism describes above. When the burning rate is very small, as is observed in the case of mixtures of benzene with tetranitromethane of zero or, all the more so, negative oxygen balance, equalizing of the composition of the surface layer and the remaining liquid can occur at a significant depth. If the layers of liquid are not great, as was the case in our experiments (10--20 diameters), then it is possible to expect that the composition of all the liquid in the process of burning can be levelled. Then, in the course of propagation of burning there will occur a change in the composition of all the liquid similar to that which is observed during the simple distillation of binary mixtures of components, with different volatility. Enrichment of liquid by the low-volatility component (in the given case, tetranitromethane) causes a corresponding change in the composition of the vapor; the relationship between quantities of fuel and oxidizer in the vapor approaches the stoichiometric for the leading reaction of burning, temperature in the flame and speed of reaction increase correspondingly, the front of the flame approaches the surface of the liquid and the burning rate is increased.

The picture considered above of the fractional evaporation of components of the mixture from the surface and equalizing of concentrations of the surface layer and the remaining liquid can be observed only at a sufficiently small burning rate. If this speed grows by any cause (increase of pressure or temperature, change of composition of mixture), then the depth at which mixing and equalizing of composition can occur during the time of combustion of a heated surface layer is decreased. At a sufficiently great burning rate the processes of fractional evaporation and the fractional burnout caused by it are developed very weakly and only during combustion of the heated layer of liquid. As a result there can appear periodic changes in the speed and character of burning. At a small thickness of the heated layer, corresponding to a great burning rate, the frequency of such changes is great, but their amplitude is very small, so that they do not play an essential role and even are not defected with the usual experimental setupe.

Fractional burnout is not observed in a series of cases and at a small burning rate. Trivial causes of such a phenomenon can be the formation of azeotropes or comparatively stable chemical compounds of components of the mixture in the liquid phase. In cases when density of the more volatile component of the mixture is higher than that of the less volatile, fractional evaporation leads to a decrease in the density of the upper layer of liquid. In such cases mixing can occur only by means of diffusion, i. e., extremely slowly. This is why we did not observe phenomena of fractional burnout, for example, for binary ZhVS of tetranitromethane with octanol and xylene, while they are clearly observed for mixtures of the same oxidizer with methanol, ethanol, and benzene. It is possible to expect further that fractional evaporation will cease to play a role in the case of burning of the explosive in conditions when reactions proceeding in the condensed phase, begin to play an essential role.

One should note that the phenomenon of fractional evaporation during burning of nonexplosive liquids was observed frequently -- for example, during the burning of such multicomponent mixtures as petroleum and certain petroleum products [3], [6] or aqueous solutions of alcohol [8].

Appearance of pulsations as a result of fractional burnout was most clearly observed in the case of solutions of poly(methyl)methacrylate in a volatile nitro ester -- methylnitrate. In the light of preceding works (see for instance [1], [9] the appearance of pulsation with an increase of viscosity appeared surprising. In the quoted works it was shown that thickening stabilizes burning and gelatinized explosives burn even in those conditions in which the same substances with low viscosity burn with pulsations. The theoretical foundations of the stabilizing influence of viscosity are known [5].

In the cases we studied the appearance of pulsations with thickening is determined by the fact that the applied polymer is much less volatile than the liquid explosive which it thickens and, at the same time, it by itself is incapable of exothermal transformation in condensed phase. During burning fractional evaporation of the heated layer occurs and the content of the volatile component is decreased. There is a corresponding increase in the viscosity of this layer, whose surface becomes a comparatively strong film, contravening further escape of bubbles of vapor. The increase of viscosity of the heated layer hampers simultaneously the equalization of its composition with all the remaining liquid. As a result of the growth of viscosity, the burning rate of the ZhVS is lowered, the thickness of the heated layer is increased and it is turned into foam with vapor bubbles, locked by the viscous film. When the vapor pressure in the bubbles becomes sufficiently great, the film is torn. With this, in zone of burning there is immediately thrown out a significant quantity of vapor, carrying with it drops of liquids which burn in the form of a flash, after which the cycle of the phenomena is repeated. The average speed of propagation of such a process can be greater than that for even burning of an unthickened substance. With an increase in the pressure under which burning proceeds the pulsation regime stipulated by the evaporation of the volatile component is suppressed. It is possible also that pulsations cease to be noticeable because of a decrease in their amplitude and an increase in frequency due to growth of the burning rate and reduction of the thickness of the heated layer.

The considered picture is observed at the comparatively great burning rate characteristic for methyl nitrate. In the case of a somewhat less volatile and slower-burning explosive -- ethyl nitrate -- the phenomenon is not expressed so clearly. During slow burning evaporation of the more volatile component can lead not to local change in the composition of the thin heated layer, but to gradual change of composition in a layer of significant thickness. Amplitude of pulsations with this is decreased. In the case of ethyl nitrate, this phenomenon leads to gradual enrichment by the polymer of a layer of increasing thickness and a fall in the burning rate, up to its attenuation at a small diameter of pipe, owing to thermal losses.

In conclusion let us note that phenomena of fractional evaporation possibly are not the only mechanism leading to variations in the speeds of burnout of separate components of a mixture. For low-volatility multicomponent systems the essential distinctions in the speeds of reactions of components can, at definite conditions, play the same role, which variations in vapor pressure play in the case of volatile explosives.

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Chapter 3 Article 31

Pages 468 - 473

A. I. Gol'binder

31. Combustion of a Hypergolic Explosive Mixture and Its Transition Into Detonation

Study of phenomena of the transition of the combustion of explosives into detonation is of essential interest in many respects. In the case of hypergolic liquid explosive mixtures we observe a number of peculiarities under the conditions of the transition of combustion into detonation; these were investigated using mixtures of tetranitromethane and organic amines, mainly aniline.

A mixture of tetranitromethane and aniline, with a composition close to the condition of zero oxygen balance, is self-ignited after a certain induction period, which under ordinary conditions (atmospheric pressure, room temperature) is close to a minute. Investigation of process, the self-ignition in particular reactions occurring during the delay period, allowed us to establish the following characteristic features of this phenomenon.

1. During the induction period the temperature of the liquid is practically the same as the initial temperature. Very slight warm-up (2--9°) is observed only at the very end of this period.

2. At the end of the induction period there begins the accelerated formation of gases. Bubbles from the latter break through the surface of the liquid, carrying with them the smallest of the drops of the liquid.

3. A strong exothermal reaction, leading to ignition, appears in the gaseous phase, or more accurately, in gas vapor droplet suspensions above the

surface of the liquid. Ignition of gases or vapor leads to combustion of the liquid mixture.

Comtustion of the self-ignited mixture propagates with considerable speed, approaching or even exceeding the stalling speed at which appears autoturbulence of the surface of combustion liquid due to the Landau effect [6].[1] Thus, in tubes 13 mm in diameter and 50 mm in length at 18--21°, the average speed of combustion of such a mixture was from 0.44 to 0.80 g/cm^2 sec. Characteristic in this case is the irregularity of propagation of combustion, strong flame pulsation and a significant (in 1.5--2 times) scatter of the time of combustion of sectors of constant length in parallel experiments. Combustion in tubes is accompanied by a sharp whistling sound. The zone of primary flame adjoining the surface of the liquid has a significant width and gleams brightly. The secondary flame above the section of the tube is hardly noticeable because of lesser brightness. Even tubes of refractory glass are noticeably fused during the combustion of the mixture, which is not observed in the case of other liquid explosives.

Just as for other explosive liquids, during transition to a pulsating regime under definite conditions it is possible to observe attenuation of combustion. In the case of hypergolic mixtures of the examined type (and this distinguishes them, for example, from nitro esters) such an attenuation is only temporary. Reactions leading to self-ignition do not stop after attenuation; the formation of active gaseous substances is continued and they again burst above the surface of the liquid. Thus, combustion of mixture of tetranitromethane and aniline (and, probably, other amines) can occur in the form of alternating bursts and

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[1] The value of the stalling speed for the given mixture is difficult to determine. We consider that it is of the same order as that determined by K. K. Andreyev [1] for nitro ester and found by us for certain liquid non-hypergolic mixtures, i.e., 0.25--0.3 g/cm^2 · sec.

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alternations. In individual cases combustion gaps attain 0.5--1.5 sec. in others, they are so small that by visual observation it is impossible to note them.

The examined mixture is capable of self-ignition and combustion in a considerably wide range of concentrations. The highest combustion rate is observed in the case of a mixture containing nearly 20% of aniline by weight (the zero oxygen balance corresponds to an amount of 15.5% of aniline by weight). Further experiments were conducted with a mixture the composition which corresponds to the maximum of the combustion rate.

In many cases, the combustion of a self-ignited mixture of tetranitromethane and aniline changed into detonation. To reveal the conditions of this transition a series of experiments were conducted in which the total mass of the prepared mixture and the height of a layer of it in the pipe were changed.

In these experiments, tetranitromethane and aniline taken in such quantities that the contents of the latter in the mixture would be 19.5% by weight were simultaneously poured into a glass tube through a common funnel. Ignition occurred within 35--55 sec. In part of the experiments the mixture burned to the end; in others, detonation occurred. The results of these experiments are shown in Table 1. The height of the detonating layer of mixture was determined by length of imprint on a metallic plate, in contact with which was a tube.

From the data of the Table it is clear that combustion of the self-ignited mixture changes into detoration if the height of the layer of liquid exceeds a certain critical magnitude. Comparing the results of experiments in tubes of different diameter, it is not hard to be convinced that namely the height of the liquid layer, and not its total mass, is the critical condition for the transition of combustion into detonation.

Experiments established also the time from the moment of self-ignition to the occurrence of detonation, and the length of the ignited layer of mixture, as the difference between the original height of the column of liquid in the tubes and the length of the imprint on the metallic plate. When combustion changed into an explosion, we did not detect any regularity in the change of the length of the liquid section burning before the occurrence of detonation. In some of the parallel experiments it was possible to observe detonation practically at the moment of ignition, but in other experiments detonation occurred after burning within several seconds.

With the growth of initial pressure, the burning time of a layer of mixture of a definite height is considerably reduced (the burning rate increases), but the transition of burning into detonation is relieved abruptly. In a series of experiments conducted in paper tubes of about 7 mm diameter, glued with waterglass, for a height of the layer of mixture of only 4 cm, we obtained the results shown in Table 2.

Other studied amines behave in a mixture with tetranitromethane, similarly to aniline. The delay time of self-ignition and the burning rate of mixtures of tetranitromethane with o-toluidine are close to those of corresponding aniline mixtures. The critical height of the layer of mixture in the glass tube, at which combustion transforms into detonation, in the case of o-toluidine, is also close to 10 cm. Mixtures of xylidine[1] and tetranitromethane are self-ignited with a delay of about 1.5 sec.; burning occurs still faster than for the mixture with aniline, with accelerated oscillations of speed, separate bursts and flame pulsations. With such a method of combustion it is very difficult to speak of any particular characteristic speed of propagation of the latter. Numerous experiments with mixtures, containing from 11.5 to 37% by weight of xylidine

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[1] Technical mixture of isomers.

(zero oxygen balance corresponds to 14.7% xylidine by weight), with total volume of liquid of explosive from 1.0 to 50 milligram, showed that regardless of the quantity of mixture it burns up to the end, if the layer height of explosive is not greater than 3 cm. With a great height of the layer, ignition regularly leads to detonation.

Table 1

Combustion of a Mixture of Tetranitromethane and Aniline (80.5:19.5) at Different Layer Heights

Внутренний диаметр трубки мм 1)	2) Объем смеси мл	3) Высота слоя смеси см	4) Частость детонации *
10	3,5	5	0/5
13,5	7,0	5	0/5
18	12,7	5	0/3
10	4,9	6	0/3
21	49	14	0/5
5,6	3,5	14	1/4
13,5	21,0	15	0/3
21	50	14	1/4
8	8,8	18	2/4
8	10,9	22	3/4
10	21	27	1/1
5	5,9	30	8/8
8	14	28	3/3
10	22,1	28	2/4
5	7,9	40	2/2
10	35	45	3/3
8	26	52	3/3
10	42	53	4/4

*The numerator is the number of cases of detonation, and the denominator is the number of parallel experiments. 1) Internal diameter of tube in mm; 2) Volume of mixture in ml.; 3) Height of a layer of mixture in cm; 4) Frequency of detonation.

Table 2

1) Начальное давление кГ/см^2	2) Время сгорания слоя высотой 4 см в сек.		5) Частость детонации
	3) минимум	4) максимум	
1,0	16,0	20,2	0/8
1,8	0,18	7,0	2/8
2,2	0,24	0,84	4/8

1) Initial pressure kG/cm^2; 2) Burn-up time of layer in height 4 cm/sec; 3) Minimum; 4) Maximum; 5) Frequency of detonation.

In the case of a mixture of triethylamine and tetranitromethane self-ignition occurs with a short delay. It is impossible, therefore, without special devices to mix, during the delay time, any significant amounts of fuel and oxidizer. During simple simultaneous pouring, the components do not mix and are simply scattered during ignition of a small portion of them which form a mixture. Ignition occurs in the form of a very sharp flash. In those experiments where by means of cooling of components or dilution of triethylamine the delay time was somewhat increased even at a height of the layer of 1.5--3 cm, a strong explosion occurred during self-ignition.

Discussion of Results

The essential role of the height of liquid column in process of transition of combustion into detonation can, in the given case, be explained as follows.

In a self-ignited and burning mixture reactions are continued between tetranitromethane and amine, as a result of which gases are formed. Gas bubbles rise to the surface of the liquid and cause a disturbance (breakaway of drops, appearance of relief). Should one consider that reactions leading to gas formation, occur more or less uniformly in its entire volume of liquid, then it is obvious that the greater the quantity of bubbles passing per unit time through a unit of surface area of the liquid, the higher the layer of liquid.

Starting with a certain critical height of the layer, the flow of gas over the surface of the liquid causes its intense dispersion and formation of a rather thick layer of gas-drop suspensions subsequent to the explosion; according to Andreyev [2] this is the cause of transition of combustion into detonation.

For confirmation of the considered mechanism special experiments were conducted, in which a varying intensity of the stream of gases could be obtained with an identical and sufficiently small height of the liquid column. A mixture of tetranitromethane and aniline, of the same composition as in the main series of experiments, was prepared in an amount of 2 ml in a tube with an internal diameter of 5 mm, and in an amount of 25 ml in a tube 18 mm in diameter. In both cases the height of the liquid column was 10 cm and in all experiments (6 apiece with tubes of each diameter) the mixture burned to the end. Then the experiments were repeated in a combined tube, the bottom part of which, approximately 4 cm long, has a diameter of 18 mm, while the upper part is 5 mm in diameter. The quantity of the mixture (11.5 ml) was selected in such a way that the total height of the layer in the combined tube was also 10 cm. With these dimensions the intensity of the flow of gas bubbles through the surface of liquid should be the same as in the tube of constant diameter with a mixture layer height of 50 cm. In all 5 experiments in the combined tubes the combustion of ignited mixture passed into detonation, which always started in the narrow part of the tube.

In the case of a hypergolic liquid explosive mixture, the gases that form and burst through the surface of the liquid are, as was shown, active products capable of fast exothermal reaction. This circumstance determines the mechanism of the flash of gas-drop suspensions and stipulates the possibility of additional strengthening of the dynamic action of such a flash due to **simultaneous** ignition above the surface of liquid and inside the bubbles, approaching it, or of a simultaneous flash in a number of bubbles, divided by thin layers of liquid.

As the experiments described here show, liquid hypergolic mixtures will behave like initiating explosives regular transition of combustion into detonation is observed in definite conditions at atmospheric pressure.

Besides the above mentioned phenomena which facilitate the formation and flash of a layer of gas-drop suspensions and increase its intensity, the presence of gas bubbles in liquid should considerably increase the sensitivity of the latter to the influence of rapid rise of pressure. Well known are the data, for example, given by F. Bouden [4] about how much the presence of gas bubbles increases the sensitivity of liquid explosives to the mechanical. A similar role is also played by the bubbles when the suspension flash acts on liquid explosives. Evidently in this case, when the bubbles are filled not with air, containing an insignificant amount of vapor from the explosives, as, for example, in the case of nitroglycerine, but with a reactive mixture of gases (vapor) in a state close to self-ignition, a relatively weak rise of pressure is sufficient to cause ignition in the bubbles. Simultaneous ignition in a series of bubbles (as a result of flash suspensions above the liquid layer) leads to detonation.

A unique variant of gas-liquid suspensions in the considered systems can be the formation of a layer of foam of bubbles of the contributing gases, separated by films of liquid explosive. If the height of the foam layer exceeds a certain minimum, its burning can become detonation as a result of the combination of weak shock waves, by a mechanism analogous to that of the triggering of detonation in gases [5]. Detonation of a foam layer causes explosion of the liquid mixture. The sources of weak shock waves can be either gas-dynamic acceleration of the burning of the foam due to the progressive growth of the surface of the burning liquid, or several consecutive flashes of gas in separate foam bubbles.

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Confirmation of the fact that a explosion appears in foam layer, can be deduced from the following indirect data: in many cases, when detonation of mixture occurred, then on the plates to which the tubes were fastened it was possible to note a sharp change of "imprint" intensity. On the section adjoining the upper part of the tube, we observed a relatively weak mechanical action, but in the lower part we noted significantly stronger action. It is possible to assume that the weak imprint was obtained on the section of foam explosion which compared to the liquid, is a small density charge[1].

The concept of triggering of an explosion in a gas or in a two-phase layer is in good agreement with the results of experiments at various pressures (Table 2). With the growth of the initial pressure the triggering of liquid explosion is facilitated, similar to that which was observed by K. K. Andreyev and V. P. Maslov [3] or E. V. Rdultovskaya and Yu. B. Khariton [7] for explosions of detonating gas.

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[1] Through no fault of the authors, it was impossible to measure the speed of detonation on various sections of a charge.

Tape No. MT-63-254

Chapter 3 Article 32

Pages 474 - 492

I. Ya. Petrovskiy and L. V. Volkov

32. On the Causes of Incomplete Detonation of Explosives in Blast Holes

During explosive work in mines cases of incomplete detonation of a charge of explosive in blast holes are often observed. This interferes with normal operations. Incomplete detonation of even a few charges lowers the effectiveness of explosive drilling work, since it disturbs the calculated diagram of interaction of charges in the face. Besides, and this is most important, it has a direct relation to two main sources of traumatism resulting from explosive works.

It is known [2] that about 40% of the cases of this type of traumatism are connected with the liquidation of the refusing charges, with their explosion during counterboring of face, with the striking of cases of explosive in loading machines, etc. Besides, incomplete detonation is a cause of burnout of explosive charges in blast holes -- an extremely dangerous phenomenon in mines with gaseous dust regimes. Explosion of part of the charge develops in the closed cavity of the blast hole a high pressure of gases having a high temperature. In these conditions, as was proven by investigations MakNII [Makayevka Scientific Research Institute for Mine Safety] [1] and a number of foreign works, all explosive can burn. If on the expiration of a certain time the cavity of the blast hole is uncovered, then burning mass is thrown out into the space near the face; whose atmosphere to this time often becomes explosive, even if it and was not before the beginning of blasting. Certainly, far from every case of incomplete detonation leads to the appearance of burnout. For that it is necessary that the cavity of the blast hole was not uncovered by the explosion of part of the charge and that the given explosive possesses a significant inclination to burning.

The practice of drilling and blasting allows to make the following general conclusions which, should be same as a basis for setting up investigations of concrete causes of the appearance of incomplete detonation.

1. Incomplete detonation is characteristic mainly for sinking works, where long charges are applied.

2. Incomplete detonation is observed more frequently with the use of explosives with relatively low detonation ability.

3. Incomplete detonation is most characteristic for coal mines, while at the same time when in mining industry, and abroad also in the coal industry, this phenomenon is rare.

Apparently, last circumstance is a consequence of essential distinctions in the technology of drilling and blasting work in the coal industry of USSR, namely:

here are used explosives having comparatively low detonational ability;

in the mining industry, and abroad also in sinking work in mines, drill boring is applied, which assures that the blast holes obtained are well cleaned of bore meal, while in coal mines blast holes are drilled in the sinking face by electric drills, for which reason they are poorly cleaned of bore meal;

in mining industry wide use is made of cutting and crushing of cartridges during their insertion in blast holes, which is forbidden in the native [Soviet] coal industry.

Investigation of the phenomenon of incomplete detonation and burnout of charges in blast holes is the subject of a series of foreign works (Tefenel and Dotrish, Fripia, Grimshaw, Odiber, Dwight, Sartorius) and in the Soviet Union (Rudakovskiy, Dubnov, Galadzhiy). It has been established that a number of factors operate under production conditions (such as improper insertion of cartridges, formation between them of corks or plugs of bore meal, a lateral or radial gap between the charge surface and the walls of the blast hole, etc.); these factors can lead to incomplete detonation even with normal quality of explosive. To prevent the latter in coal mines two measures were passed which in their time were given great significance. In the first place a rule was introduced prohibiting crushing of cartridges in blast holes and requiring that they be inserted in the blast hole by a solid core. This was intended to avoid the formation of plugs of bore meal between the cartridges; this, if judging by the data of MakNII [1], is the main cause of incomplete detonation. Secondly, to increase the detonation ability of the charge the diameter of the cartridges was increased from 32 to 36 mm. Subsequent practice of drilling and blasting works did not show, however, the expected sharp lowering in the number of cases of incomplete detonation and burnout of charge. This led to the conclusion that the cause of incomplete detonation of blast hole charges is more complicated and requires more detailed study. In connection with this in 1957--58 authors in the former Pan-Union Scientific Research Coal Institute (VUGI) conducted work [5], whose results are briefly examined in the present article.

Influence of Magnitude of Air Gap Between Faces of Cartridges On Transmission of Detonation

Ammonite No. 8 and Pobedite PU-2 in cartridges with diameters of 32 and 36 mm were investigated. The weights were 200 and 250 g and the density of explosive in the cartridge 0.98--1.02 g/cm^3 respectively. The critical diameter by our determinations, was for Ammonite No. 8, 12 mm, and for Pobedite PU-2, 8 mm. Distances of transmission of detonation on standard methodology[1] are given in Table 1.

As blast hole models we used steel pipes with a wall thickness of 3 mm. Internal diameter of pipes in tests of cartridges 32 mm in diameter was 36 mm, and for 36 mm cartridges, 39 mm. To eliminate the gap between the lateral surface of

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[1] Quantity of confirmations was increased from 3 to 10 experiments per point.

the cartridge and the pipe walls, the cartridges were encased in cardboard. Stemming was not used. The completeness of detonation of a passive cartridge was judged by the character of destruction of the pipe and the absence of residue of explosive. The adequacy of such a criterion was proven by comparison of results of experiments with compression of standard leaden columns, placed behind the face of a passive cartridge. Sections of pipes between active and passive charges were not destroyed and were not bulged during explosion.

Table 1

Distance of transmission of detonation through air gap for Ammonite No. 8 and Pobedite PU-2

1) Наименование ВВ	2) Диаметр патронов мм	3) Расстояние передачи детонации через воздушный промежуток в см	
		4) На открытом воздухе	5) В стальной трубе без зазора
6) Победит ПУ-2	32	5	48
6) Победит ПУ-2	36	10	>100
7) Аммонит № 8	36	3	14

1) Designation of explosive; 2) Diameter of cartridges,mm; 3) Distance of transmission of detonation through air gap in cm; 4) In the open air; 5) In steel pipe without gap; 6) Pobedite PU-2; 7) Ammonite No. 8.

The maximum distances, at which we observed faultless transmission of detonation (confirmed by 10 repetitions) are given in Table 1.

At large distances a very slow buildup of probability of refusal is observed. Thus, Ammonite No. 8 in cartridges with diameters of 36 mm gives this frequency of transmission of detonation: at 14 cm — 100%, 15 — 90%, 20 — 64%, 30 — 55%, 40 — 33%.

The sharp increase in distance of transmission of detonation with location of the charge in a pipe is explained by the fact that the shock wave and products of explosion, being propagated in the pipe, preserve their speed and pressure much longer than in the open air and, consequently, can trigger cartridges of explosive at significantly large distances. This is illustrated by photographs obtained with the help of an SFR instrument of mirror observation. In Fig. 1 is shown the propagation of detonation products from the face of active cartridge in the open air, and in Fig. 2 — in a steel pipe. It is very clear that in pipe the speed of products of explosion is lowered slowly, but in the open air — fast. The more the explosion products can expand to the side (i.e., the greater the ratio of pipe diameter to the diameter of the cartridge), the closer the picture of the phenomena will approach that of transmission of detonation in the open air. Small distances of transmission of detonation[1] obtained by MakNII [1] in a steel mortar, are explained, apparently, by the fact that the channel of the mortar had a very large diameter.

The results of the experiments allow to note the following.

1. Distance of faultless transmission of detonation in pipes is significantly greater than that in the open air (for Ammonite No. 8 — close to 5 times, and for Pobedite PU-2 — 10 times).

2. Replacement of ammonite without nitroglycerine by a low-percentage nitroglycerine explosive practically liquidates the danger of appearance of incomplete detonation of charge due to improper insertion of separate cartridges (in the absence of other causes), since improper insertion at distances of 50 and 100 cm in practice is doubtful.

3. Standard test of transmission of detonation in the open air not only does not give absolute data on the distances of transmission of detonation in blast holes, but also does not show the correct relationship among these distances for different explosives. Therefore the standard test should be considered only as a means of control of quality of each given explosive.

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[1] Near to distances of transmission of detonation in the open air.

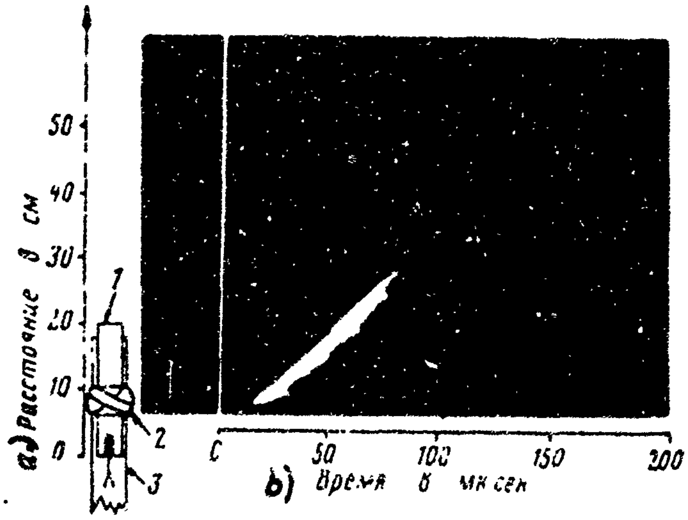

Fig. 1. Movement of shock wave and products of detonation from end of active charge in the open air. (Ammonite No. 8: diameter of charge 36 mm, weight 200 g, density 1.0 g/cm^3). 1 — charge, 2 — insulating tape, 3 — wooden plate; a) Distance in cm; b) Time in microsec.

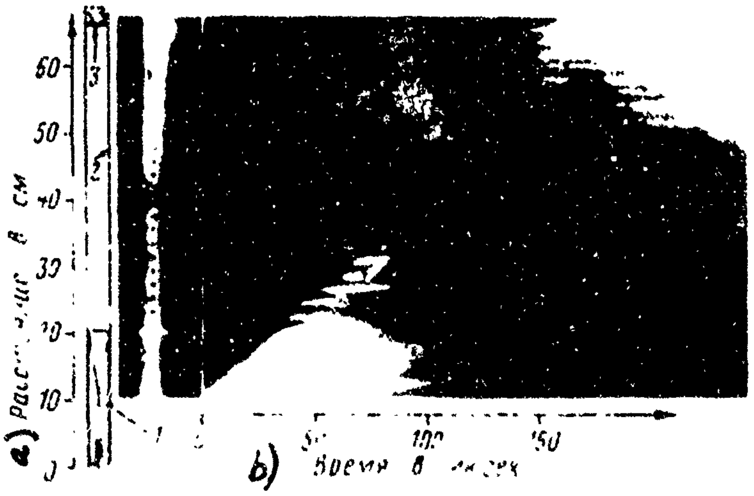

Fig. 2. Movement of shock wave and products of detonation from end of active charge in a steel pipe. (Ammonite No. 8: diameter of charge 36 mm, weight 200 g, density 1.0 g/cm^3). 1 — charge; 2 — steel pipe 39 mm in diameter with a series of apertures for survey; 3 — steel plate. a) Distance in cm; b) Time in microsec

Influence of Magnitude of Bore Meal Plugs Between Cartridges On Transmission of Detonation

First we determined the length of the plugs that can be formed during insertion of cartridges through poorly cleaned blast holes. For that through a block of rock we drilled blast holes 45 mm in diameter with an electric core drill. Blast holes practically were not cleaned of bore meal, if one ignores the removal of a certain quantity of it during extraction of the boring rod. The bore meal was dry. Through these blast holes we pushed cartridges with a diameter of 36 mm. The length of the dust plug collected ahead of the cartridge usually did not exceed 2 and, in very rare cases, 2.5 cm (measurement was made after compression of the plug by the cartridge).

Analogous experiments were also conducted in VUGI under the leadership of N. G. Petrov [3]. From a series of alabaster copies of blast holes, drilled in a mine, the sample was selected with the biggest distortions and a cement split model of the blast hole was prepared from it. In the channel of this model bore meal was poured and pushed through by cartridges of explosive. Just as in our experiments, dust plugs with a length of more than 2—2.5 cm were not observed.

In the works of MakNII [1] cartridges of Ammonite No. 8, 32 mm in diameter, in the mortar gave 8% refusals with a plug of coal dust in 1 cm in length, but with such a plug of inert dust — 56%. A coal-dust plug of 3 cm length gave 100% refusals. Pobedite No. 6 with a coal-dust plug 1 cm in length gave 12% refusals, but at 3 cm — 88%.

In order to determine whether the small distances of transmission of detonations obtained by MakNII were connected with the presence of a radial gap between the cartridges and the walls of the blast hole, we conducted experiments in the absence of this gap.

The tests were conducted in steel pipes. As material of the plug we applied sand, clay schist, and coal. The plug was packed by a force up to 5 kg and occupied all the space between cartridges. The radial gap was filled by cardboard; stemming was not applied.

With an increase in the length of the plug the probability of transmission of detonation is lowered very fast. Thus, for example, for Pobedite PU-2 with a cartridge diameter of 32 mm this is confirmed by the following data:

Length of sand plug in cm	5.2	5.5	6.0
Frequency of transmission of detonation in %	100	80	66

Results of tests, confirmed by 10 repetitions, are given in Table 2.

Table 2

Transmission of detonation through different dust plugs in the absence of radial gap between charge and walls of blast hole

Наименование ВВ 1)	Диаметр патронов *мм* 2)	3) Предельные расстояния безотказной передачи детонации через пересыпки в *см*		
		4) Песок	5) Сланец	6) Уголь
7) Победит ПУ-2	32	5,2	6,0	3,5
	36	5,2	—	—
8) Аммонит № 6	32	3,2	—	—
	36	3,5	—	4,5

1) Designation of explosive; 2) Diameter of cartridges, mm; 3) Maximum distances of faultless transmission of detonation through dust plug, in cm; 4) Sand; 5) Schist; 6) Coal; 7) Pobedite PU-2; 8) Ammonite No. 8.

From Table 2 it follows that the maximum distance of transmission of detonation through a dust plug changes very little with a change in cartridge diameter. Hence it is clear that changing to cartridges of large diameter, without an increase of requirements of technical conditions by the index of transmission of detonation on air[1] will worsen its transmission through a dust plug in a blast hole. The transition of drilling and blasting operations in mines to cartridges of increased

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[1] Such an increase in essence would be a requirement for preservation of explosive quality at the former level, since the distance of transmission of detonation in the standard test strongly depends on the diameter of the explosive cartridges.

diameter was performed without any changes of technical conditions for the explosive and therefore did not lead in practice to a lowering of the number of cases of incomplete detonation and burnout of charge in blast holes.

The question arises of the mechanism of transmission of detonation with dimensions of the dust plug near to the maximum. Is the passive charge triggered by the shock wave passing through the plug, or does the plug initiate the explosive by the impact of its whole mass? To ascertain this we conducted the following experiments.

Cartridge of Ammonite No. 8, 36 mm in diameter were inserted in a steel pipe without a radial gap. The active cartridge was closely adjoined by a plug 2--2.5 cm in length, i.e., less than the maximum. Between the plug and the passive cartridge was left an air gap of 10 cm, i.e., also a little less than the maximum. In wall of pipe at the air gap section we drilled 20 apertures 10 mm in diameter to decrease the compression ratio of air during movement of the plug. In all experiments detonation was transmitted completely. This speaks in favor of the mechanism of transmission of detonation by the impact of the entire mass of material, since the air gap in combination with the plug abruptly weakens the shock wave, but has little influence on the momentum of center of gravity of the plug. An increase in the air gap to 30 cm led to refusals. Analogous results were obtained without the apertures in the pipe.

There are other arguments favoring our expressed assumption on the mechanism of transmission of detonation through a plug between cartridges of charge in a blast hole. If transmission of detonation through the plug occurs as we assume, then the mass of the maximum plug, appearing per unit of area of charge cross section should be near for various materials. Data of the corresponding calculation are given in Table 3.

Thus, our assumption is confirmed with an accuracy ±15% for Pobedite PU-2 and ± 22% for Ammonite No. 8

Table 3

1) Наименование ВВ	2) Диаметр патронов мм	3) Удельная масса предельных пересыпок в г на см² поперечного сечения заряда		
		4) Песок	5) Сланец	6) Уголь
7) Победит ПУ-2	32	8,2	9,0	6,8
8) Аммонит № 8	36	5,7	—	3,6

1) Designation of explosive; 2) Diameter of cartridges, mm; 3) Specific mass of the maximum plug in g per cm^2 of the charge cross section; 4) Sand; 5) Schist; 6) Coal; 7) Pobedite PU-2; 8) Ammonite No. 8.

Apparently, the decisive value in such mechanism of transmission of detonation is that of the momentum of the plug. The momentum communicated to the plug by the explosion of a given explosive,in our conditions is kept approximately constant for all magnitudes of the plug, since it is determined mainly by the time of bursting of the pipe walls. Therefore with an increase in the plug its momentum changes in inverse proportion to the mass and, reaching a known limit, ceases to excite detonation in the passive charge.

In Fig. 3 are given photographs, obtained by means of an SFR, of transmission of detonation in steel pipes through maximum plugs of sand between cartridges of Ammonite No. 8 having diameters of 36 mm. Delay time of transmission of detonation through the plug will attain 70 microsec.

For an open charge, where the free dispersion of products of explosion abruptly lowers the pulse received by the plug, we obtained 100% refusals of transmission of detonation through a plug of a magnitude of 1 cm, both for Ammonite No. 8 and for Pobedite PU-2.

In the light of the above it may be easy to explain the sharply reduced magnitudes of the maximum plug obtained in MakNII: the main tests there were conducted with very large radial gaps, approximating the character of the phenomenon of transmission through a plug in the open air. It is unsurprising that in MakNII refusals were obtained even with a plug of 1 cm. The influence of such a small plug was assessed as decisive, inasmuch as they are very probable in industrial conditions.

By our data, the magnitude of the maximum plug with which no refusals in transmission of detonation are observed in the absence of a radial gap, significantly exceeds the magnitude of the probable plug met in industrial conditions. From this it follows that the practically possible plugs, with elimination of the radial gap (for example by means of cutting and crushing of cartridges during insertion in blast holes), cannot by themselves give that frequency of incomplete detonations of blast hole charges that is observed in mines at present.

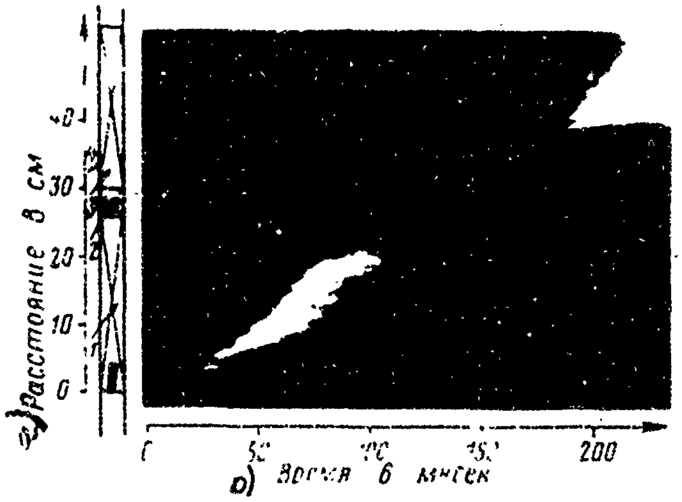

Fig. 3. Transmission of detonation in steel pipe, in the absence of a radial gap, through a sand plug 3.5 cm in length. (Ammonite No. 8: diameter of cartridge 36 mm, weight 250 g, density 1.0 g/cm³). 1 -- active cartridge; 2 -- plug; 3 -- passive cartridge; 4 -- steel pipe; a) Distance in cm; b) Time in microsec.

In spite of this question, the struggle with the possibility of formation of plugs between the cartridges a blast hole charge remains very urgent. A radical solution of this question would be the adoption of washing during rotary drilling of blast holes; this has been initiated in mines of the Kuznetsk Basin. There are other expedient methods, as for example:

a) Adding to the faces of the explosive cartridges convex (streamlined) forms. Such cartridges will not gather large plugs before themselves.

b) Development of simplest attachments for improvement of cleaning of blast holes.

c) Increasing the diameter of rods, with maximum approach to the diameter of the cutter, and banning the use of rods after definite wear.

d) Application of cylindrical cutters, decreasing distortion of blast holes during drilling.

e) Application of explosives which have large distances of transmission of detonation through plugs.

On The Incomplete Charge Detonation Due to The Inclusion in Them of Cartridges With Lost Detonation Ability

A cartridge of explosive with lost detonation ability, occurring in the charge, acts as a plug 20--23 cm in length and must necessarily lead to incomplete detonation.

An explosive cartridge can lose its detonation ability in a wet blast hole as a result of soaking. To prevent this one should apply waterproof explosives. In USSR several methods have been developed of making explosives waterproof fully sufficient for the majority of working conditions met in the coal industry. The time has come to issue overwhelming quantities of explosives in waterproof variants.

Cartridges can lose detonation ability also during transportation and storage in the warehouse. Ammonite not only has relatively low detonation ability, but also quickly loses it due to moistening and matting during storage, especially at increased humidity and variations of temperature. Paraffined shells partially help resist these harmful phenomena. However, during protracted transportation of explosives from factories to consumers in separate cartridges there appear small, difficult-to-detect disturbances of the airtightness of the shell. During subsequent storage in a warehouse such cartridges lose detonation ability much faster than those with unimpaired shells. If in the stored lot of explosives such cartridges make up several percent, then they are almost never detected during tests on the transmission of detonation, i.e., they are difficult to control. But even 2% of such cartridges will give during blasting an average of two refusals in every drift. In connection with this, the phenomenon of loss of detonation ability by individual cartridges causes industry more harm than a general, even lowering of detonation ability by entire lots, which is easily detected.

To reduce the possibility of such phenomena it is necessary to improve the sealing of explosives and to lower the actual periods from the moment of manufacture of explosives to their use.

At present, cartridges during their issue to demolition experts are pierced by needle-shaped stamps, which disturbs their airtightness. Unused cartridges are returned to underground mine storehouses and there fast lose detonation ability. It is necessary to reject the perforation of explosive cartridges in mines and to introduce printing of number signs on the shell of cartridges during the manufacture of explosives at the factory.

One should expand application of explosives containing up to 10--15% nitro ester and therefore possessing increased detonation ability, which is retained longer during storage.

In connection with the fact that for Soviet Union prolonged periods of storage of explosives are characteristic, it is very important to reduce their deterioration during storage. In this respect, it is expedient to use the results of work conducted in England [7] and Poland, where a positive effect was obtained by the introduction in the composition of explosives of a small quantities of certain substances (for example, fuchsin).

Influence of Radial Gap Between Lateral Surface of Cartridges And Walls of Blast Hole

The gap between the lateral surface of the explosive cartridge and the walls of the blast hole, called the radial for short, can lead to attenuation of charge detonation, even while the cartridges have normal detonation ability in air and are inserted in the blast hole end to end, without any dust plug. This phenomenon was investigated by S. I. Rudakovskiy (1938), A. Ye. Pereverzev and A. A. Il'yushin (1947), and L. V. Dubnov (1954).

Several hypotheses are offered to explain the mechanism of this phenomenon. Most probable cause of attenuation of detonation consists in the fact that products of explosion, being propagated in the gap with a speed exceeding that of detonation, pack the explosive ahead of the detonation wave front.

For the investigations described below we applied Pobedite PU-2 from the lot used in the preceding experiments and Ammonite No. 8 from a new lot, which appeared somewhat better than the former (distance of transmission of detonation by standard methodology, but with 10 repeated tests per point, was 4 cm for cartridges 32 mm in diameter and 5 cm for 36 mm cartridges; for the former lot it was 3 cm for a diameter of 36 mm).

Experiments were conducted in steel pipes with internal diameters of 39 mm for 32 mm cartridges and 44.5 mm for 36 mm cartridges, i.e., the radial gaps were selected as near as possible to those existing in production. Thickness of walls of pipe was 3 mm. A charge of Ammonite constituted three cartridges, and a charge of Pobedite four. The cartridges were disposed end to end in the pipe. From side of the striker stemming was not used; the opposite end of the pipe was, in most cases, packed to 5—7 cm with a mixture of sand and clay or placed on a massive steel barrier[1]. The results of the tests are shown in Table 4.

The data in Table 4 show that even by itself, without complicating circumstances, the radial gap can lead to incomplete charge detonation of Ammonite

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[1] As was shown by the experiments, this stemming had no influence on the frequency of refusals.

and Pobedite of normal quality.

Table 4

Incomplete detonation of explosive charges in steel pipes in the presence of a radial gap

1) ВВ	2) Диаметр патронов мм	3) Количество опытов	4) Количество полных детонаций	5) Количество неполных детонаций *	6) % неполных детонаций
7) Аммонит № 8 (3 патрона)	32	18	3	15	83
	36	5	4	1	20
8) Победит ПУ-2 (4 патрона)	32	4	2	2	50
	36	9	9	0	0

*Breakoffs of detonation in charges of Ammonite No. 8 occurred most frequently at the third cartridge (sometimes even at the end of the second), but in charges of Pobedite PU-2 — only at the fourth cartridge.

1) Explosive; 2) Diameter of cartridges, mm; 3) Number of experiments; 4) Number of full detonations; 5) Number of incomplete detonations*; 6) % incomplete detonations; 7) Ammonite No. 8 (3 cartridges); 8) Pobedite PU-2 (4 cartridges).

From Table 4 it also follows that the appearance of incomplete detonation charge depends on the properties of the explosive, the diameter of the cartirdges and the length of the charge. Ammonite No. 8 gives incomplete detonations significantly more frequently than Pobedite PU-2. For both explosives a decrease in cartridge diameter leads to an increase in the probability of breakoff of detonation.

It is especially important to note that the probability of breakoff of detonation increases with an increase in charge length. If charges of Ammonite No. 8 were to consist of two cartridges, the cases of incomplete detonation would be significantly more rare, because the majority of breakoffs for that explosive occurred at the third cartridge. But if charges of Pobedite PU-2 were made up of not four, but three cartridges, the cases of incomplete detonation for it in general would not be fixed. This corresponds to practical data, where the overwhelming majority of cases of incomplete detonation occur during the application of long charges (for example, in sinking work).

In our experiments incomplete detonation occurred significantly more frequently than under production conditions. This means that the considered phenomenon is strongly affected by the conditions of the experiments.

For more detailed clarification of the mechanism of breakoff of detonation we conducted several series of experiments.

With the help of an SFR instrument in the regime of a magnifier of time (frame photography) we photographed the process of detonation of an explosive charge in steel pipes in the presence of a radial gap (Fig. 4). A pipe with an internal diameter of 39 mm was disposed horizontally. Along the upper and lower generatrices of the pipe we drilled apertures 4 mm in diameter. A charge of Ammonite No. 8, 32 mm in diameter was disposed inside the pipe with a radial gap adjoining the lower row of apertures. Therefore in the lower apertures the gases begin to escape only after passage of the detonation wave. The advancing flow of gases, being moved along the gap, is detected with the help of the upper row of apertures.

The pipe, pasted with paper with black stripes against the apertures, was photographed to explosion on all frames and served thus as a scale and reference point. During explosion the exposure rate was 150,000 frames/sec. In Fig. 4 are shown only 4 frames, selected with intervals 40 microsec. The distance between adjacent stripes on the pipe was 2 cm. The speed of the front of escaping flow of explosion products in the gap was, in the mean, 3500 m/sec, and the speed of detonation — 2700 m/sec. In Fig. 4 it is clear how leading increases from 8 cm on the first frame to 18 on the fourth. This fast flow of gases possesses high pressure and can compact the explosive ahead of the detonation wave. With such compacting there is not only an increase in the density of the explosive, but also a decrease in the diameter of the cartridge.

It is known that for a mixture of explosives with an increase in charge density the detonation ability is lowered (critical diameter is increased). Therefore during compacting of cartridges by the advancing flow of gases their diameter can become less than the critical and detonation will die out. This is observed in our experiments and in real conditions for industrial explosives, and also much more frequently for those explosives whose critical diameter is larger and increases more quickly with density. Just these properties distinguish Ammonite No. 8 as compared to Pobedite PU-2. By the same token refusals occur more frequently during use of explosives of lowered quality (by manufacture or from moistening, soaking, matting), since the lowering of explosive quality increases its critical diameter.

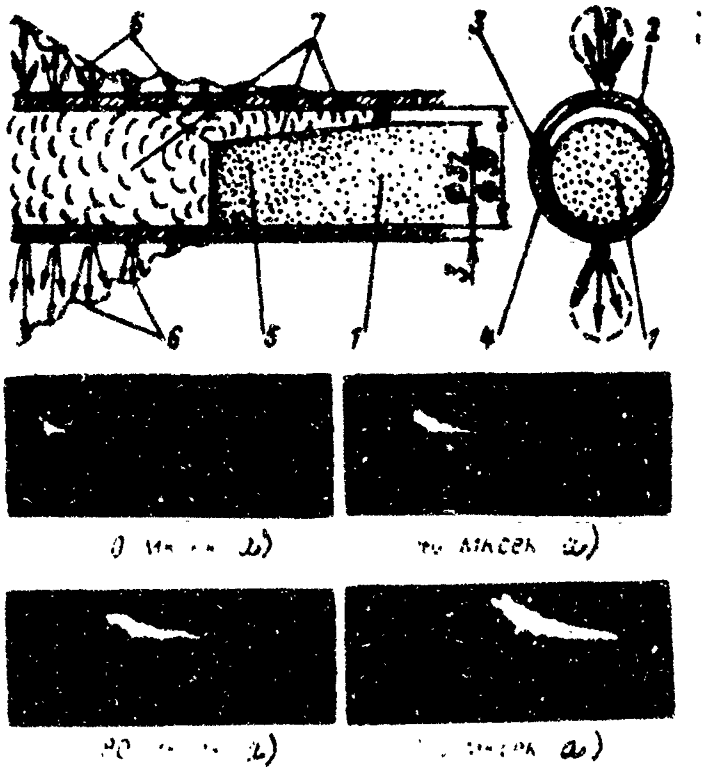

Fig. 4. Detonation of charge in pipe with gap. (Ammonite No. 8: diameter of cartridges 32 mm, charge of three cartridges). 1 — charge; 2 — steel pipe; 3 — sand; 4 — plasticine; 5 — zone of compacting; 6 — front of gas stream; 7 — products of detonation inside pipe; a) microsec. First frame is taken 50—60 microsec after triggering of charge.

The packing of the charge by the pressure of gases, moved in the gap, carries a dynamic character, since it is accomplished after small intervals of time. Therefore the degree of packing of charge obtainable to the moment of the approach of the detonation wave depends not only on the pressure of gases, but also on the time of their action, i.e. on the magnitude of leading. This explains the increase in probability of refusals with an increase in the charge length, since with this leading is increased.

A large role is played by the magnitude of the gap. With a very large gap (in limit — in the open air) the leading flow cannot be created, since gases can freely expand to all sides. With a very small gap (in limit — without gap) the leading flow meets too great a resistance and cannot considerably outstrip the detonation wave. Obviously, there exists a certain most dangerous magnitude of gap, with which the phenomenon of leading is most sharply expressed; charges which detonate faultlessly in the open air and even more so in a pipe without a gap give a great percentage of refusals with this "dangerous" magnitude of gap.

In this work we did attempt to establish the most dangerous magnitudes of gaps, but investigated only the magnitudes near to those observed in production. However, the fact that in our experiments the frequency of refusals was significantly higher than in production speaks of the great rigidity of conditions of laboratory experiments. This is explained by the fact that the pipe in which the experiments were conducted gives a straight gap with smooth walls, but in real blast holes the walls are winding. This sharply increases resistance to the movement of gases along the gap and decreases the possibility of leading. Thus, a blast hole with uneven walls is equivalent in this respect to a pipe with a smaller radial gap.

We set up a series of experiments for checking the above considerations on the mechanism of the appearance of refusals with a radial gap. If these considerations are correct, the presence of a gap should not only not disrupt, but should even help the passage of detonation in charges of explosives whose critical diameter during an increase in density does not grow, but decreases. These include trotyl, hexogen, picric acid, PETN, and so forth. We conducted experiments with trotyl of a density of 1 g/cm^3. The diagram of these experiments is presented in Fig. 5. In the open air charges of trotyl 8 mm in diameter faultlessly detonated, but with a diameter of 6 mm detonation died out, i.e., the critical diameter with this density was equal approximately to 7—8 mm. In duralumin pipe with internal diameter of 11.7 and external diameter of 16 mm detonated charges 8 mm in diameter and 50 cm long detonated faultlessly. Then we placed in the same pipe a charge 6 mm in diameter, i.e., less than the critical. In order to create in the gap a powerful flow of high-pressure gases the charge was triggered by an intermediate detonator of the same trotyl, but with a diameter of 9 mm (in the experiments in the open air such triggering was applied). Detonation proceeded all along a charge 58 cm in length. Experiment was repeated 7 times with this result, which indicates the presence of compacting of the explosive by leading gases.

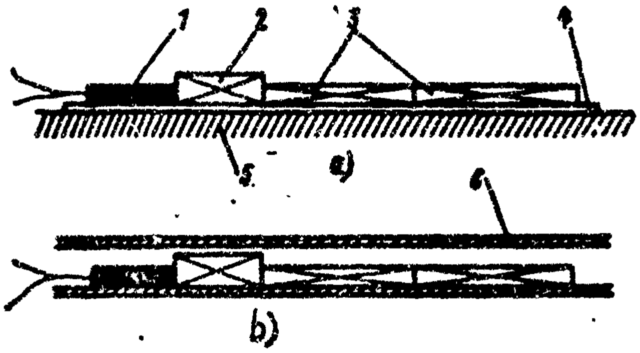

Fig. 5. Diagram of experiments on the detonation of a charge of powdery trotyl at a diameter less than the critical: a) in the open air, b) in a pipe. 1 — electrodetonator; 2 — additional detonator of trotyl 9 mm in diameter and 40 mm long, with a density of 1.0 g/cm^3; 3 — cartridges of trotyl — diameter 6 mm, length 290 mm each, density 1.0 g/cm^3; 4 — cardboard strip; 5 — steel slab; 6 — duralumin pipe with internal diameter of 11.7 and wall thickness of 2.2 mm.

Johansson [9] arrived at analogous conclusions, independently of us; in 1958 in Sweden he investigated the influence of a radial gap on the detonation of ammonium gelatin dynamite.

Let us consider now the combination of a radial gap with dust plugs between the cartridges. In production such a combination is possible, since the rule about inserting cartridges in a blast hole as a solid column is not always followed — in fact, is not always realizable. Besides, a small plug can be formed between cartridges even during observance of this rule.

We saw (see Fig. 3) that even a small plug strongly delays the propagation of the detonation wave and increases its lag from the leading flow of gases, redoubling the harmful influence of the gap. Therefore we conducted experiments to study the joint action of the plug and the radial gap. As material for the plug we used sand. In Fig. 6 is presented the diagram of these experiments. Pobedite PU-2 in cartridges 36 mm in diameter with a plug of 2 cm gave 10% refusals, but with a plug of 3 cm refusals were massive. Ammonite No. 8 in cartridges 36 mm in diameter even with plugs of 0.5--1 cm gave 11 refusals in 15 experiments.

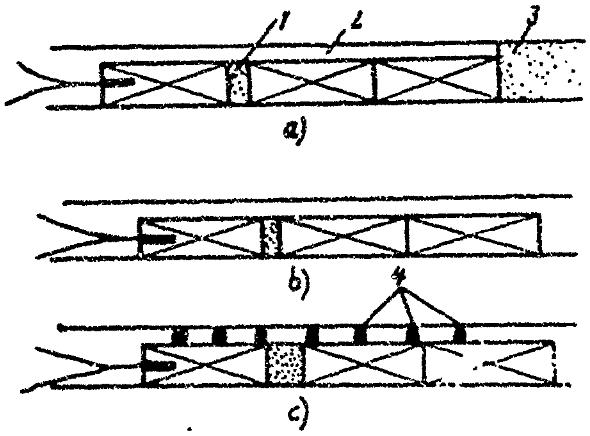

Fig. 6. Diagram of experiments to study the joint action of a plug between cartridges and a radial gap on the passage of detonation: a) with reflecting surface; b) without reflecting surface; c) with partitions in radial gap; 1 -- plug, 2 -- radial gap, 3 -- reflecting surface, 4 -- partition of insulating tape.

Light transverse walls (of wound braid of insulating tape), by blocking a section of radial gap destroyed the harmful influence of the gap: Pobedite PU-2 32 and 36 mm in diameter detonated faultlessly with plugs 4 cm in thickness while without these crosspieces such a plug led to 100% refusals. This indicates that it is sufficient to crush in the blast hole at least only an end of every cartridge in order to liquidate the harmful influence of the radial gap on the completeness of detonation.

Combination of a radial gap (if this gap is not very great) with incomplete insertion, obviously, should not strongly worsen the transmission of detonation as compared to incomplete insertion without a gap, since the leading flow of gases, being abruptly expanded in the air gap between cartridges, weakens and flows together with the main mass of detonation products moving from the face of the active cartridge. We were convinced by the experiments that in the presence of a radial gap, the distance of transmission of detonation through the air gap is not decreased.

Thus, Pobedite PU-2 32 mm in diameter in a pipe with an internal diameter of 39 mm, faultlessly transmits detonation through an air gap of 48 cm, but Ammonite No. 8, 36 mm in diameter in a pipe with an internal diameter of 44.5 mm -- 14 cm (cf. Table 1).

Thus, we analyzed the influence of the radial gap on the detonation ability of blast hole charge. We proved that the radial gap presents the main danger with respect to the appearance of incomplete detonation, leading ordinarily to the burnout of charge. Plugs especially strengthen the harmful action of the gap and are very probable under the conditions of our coal mines. The simplest and at the same time most active measure of struggle with the harmful influence of the radial gap is its elimination by means of notching the shells of cartridges and crushing them in the blast hole with a rammer. Such a method of loading should be adopted in sinking work, because there most frequently is observed incomplete detonation, and also because crushing of cartridges increases effectiveness of drilling and blasting works during driving [4]. The action of a rule requiring insertion of cartridges in the blast hole as a solid column and not to disturb their entirety, contravenes the adoption of notching and crushing of cartridges and therefore should be modified.

With the adoption of crushing it is necessary simultaneously to take measures to make all explosives waterproof and resistant to deterioration in storage; this can be attained by means of changing the composition of explosives and improving their sealing.

In drifts where short charges are applied the influence of the radial gap is small and crushing of cartridges is inexpedient, all the more so because it will, by increasing brisance of explosion, lead to undesirable excessive breaking up of the coal.

On the Detonation Ability of Blast Hole Charges of Pressed Rock Ammonite No. 1

With the adoption in the mining industry of the powerful, dangerous explosive pressed rock Ammonite No. 1 cases of its incomplete detonation in blast holes were detected. In connection with this the Joint Committee on Explosives of the Institute of Mining Affairs of the Academy of Sciences of the USSR in 1958 sent to VUGI a request to investigate the cause of this phenomenon.

For the tests rock Ammonite No. 1 was delivered in cartridges 36 mm in diameter, weighing 250 g. Every cartridge consisted of two charges with a density of 1.45 g/cm^3, located in paper cases with subsequent paraffining. Brisance of this explosive at a density of 1.0 g/cm^3 equals 20 mm, and its efficiency -- 450 cm^3.

As was already indicated; for the mining industry, where drill boring is applied, the possibility of formation of plugs in blast holes is not characteristic. In connection with high-density explosives it was difficult also to expect over-compacting of its explosion products outdistancing the detonation front in the radial gap. This was confirmed in laboratory conditions: in steel pipes with an internal diameter of 44.5 mm there were no cases of burnout of detonation in charges of rock Ammonite No. 1 composed of four cartridges.

Therefore the cause of incomplete explosions must be connected with the possibility of incomplete insertion of cartridges in combination with reverse initiation.

In mining industry fire [fuse] detonations are widely used. In order to avoid cutoff of the fuse by explosions of blast holes of the preceding series, a striker is inserted in the blast hole in a number of the first cartridges. With this one can create conditions with which part of charge is initiated through the air gap on the same side as the striker, from which into it is inserted a percussion cap (reverse initiation). To check the influence of the air gap in combination with reverse initiation, we conducted experiments in steel pipes 39 mm in diameter without removal of the radial gap. Results of these experiments are given in Table 5. Besides, it shows data on the transmission of detonation through an air gap in the open air and also through a plug in the open air and in pipes. Investigation of transmission of detonation through a plug were undertaken for the purpose of accumulation of general comparative data.

Table 5

Transmission of detonation between cartridges of pressed rock Ammonite No. 1 in different conditions

1) Условия инициирования	2) Максимальное расстояние безотказной передачи детонации, см			
	3) Через воздух		6) Через песок	
	4) на открытом воздухе	5) в трубе	7) на открытом воздухе	8) в трубе
9) Прямое	7	20	1,5	4
10) Обратное	1,5	10	—	2

1) Conditions of initiation; 2) Maximum distance of faultless transmission of detonation, cm; 3) Through air; 4) in the open air; 5) in a pipe; 6) Through sand; 7) in the open air; 8) in a pipe; 9) Direct; 10) Reverse

From Table 5 it follows that in the case of reverse initiation in a pipe with an air gap, exceeding 10 cm, refusals are obtained. Such a magnitude of incomplete insertion is fully real for industrial conditions and cases of incomplete detonation, apparently, should be explained by just this.

It merits attention that in all forms of tests conducted, reverse initiation sharply worsens transmission of detonation.

It is interesting to note also that pressed rock Ammonite No. 1, having a high index of transmission of detonation by standard methodology (on level of safety of nitroglycerine explosives), transmits detonation through a plug in a pipe worse than will Pobedite PU-2, and through an air gap in a pipe — several times worse. Thus, even powerful Ammonite with high detonation properties under blast-hole conditions yields by a series of important indices to low-percentage nitroglycerine explosives, which have a significantly smaller capacity. This gives still another example of the fact that standard tests of transmission of detonation in the open air do not reflect the behavior of explosives in blast holes.

Preliminary Check of Laboratory Investigations by Mine Tests

In the course of the fulfillment of the program of industrial tests of new explosives [6] in passing and on a limited scale a check was made of the influence of crushing of cartridges on the frequency of cases of incomplete detonation.

In the "Southern" mine of the "Rutchenkovugol" trust (Donets Basin) in July — August 1958 during the driving of a cross-cut comparative tests were conducted of a new explosive, which was first called E-3, and given the permanent name Ammonite PZhV-20.

E-3 is a highly protective explosive whose manufacture and test were proposed by VUGI. In composition it was similar to the English "Unigex" [8]. Not having a safety shell, E-3 does not ignite methane by opened charges up to 300 g in weight. Such high safety properties are attained by means of replacement of ammonium nitrate (NH_4NO_3) and sodium chloride, which are usually applied in safety Soviet explosives by exchange salts: sodium nitrate ($NaNO_3$) and chloride of ammonium (NH_4Cl). During explosive reaction there occurs cation exchange and will emanate chlorine sodium is separated in a highly dispersed state with great specific surface, which sharply increases the effect of flash. In this way it is possible, with the same safety, to attain higher energy of an explosive with exchange salts, than in an explosive with a flash extinguisher ($NaCl$) introduced into the composition in prepared form.

Replacement of ordinary components by exchange salts simultaneously practically solved in the given case the problems of deterioration in storage and hygroscopicity, because new components have low hygroscopicity and do not deteriorate. After warehouse storage for a year such an explosive had not deteriorated and retained normal quality.

Besides, the new explosive is highly waterproof, several times more so than PZhV-20, Ammonite V-3 or Ammonite No. 6 ZhV. This was attained by the introduction into its composition not only of stearate of calcium, but also sodium-carboxymethyl cellulose and kaolin. Sodium-carboxymethyl cellulose will swell very fast in water, and the cartridge will be covered by a mucous mass, stopping the access of water inside the cartridge. Kaolin will swell slower, but then it makes a more consistent gel; with this aim it is introduced.

To assure high detonation ability, into the composition of E-3 was introduced about 15% of slightly gelatinised nitroglycerine (low-freezing mixture). As a result the explosive obtained the structure of a fat, heavy powder with a density of 1.25 g/cm^3. Cartridges were easily crushed in blast holes, filling the whole section. With respect to transportation and storage the new explosive falls, as does Pobedite, into the class of Ammonite.

E-3 gives pressing of lead columns of not more than 7—7.5 mm and has an efficiency of about 185 cm^3. However, because of the increased density of the explosive and crushing of cartridges there was attained a high concentration of energy per unit of volume of blast hole, which allowed to preserve specific expenditure of drilling on the same level as for PZhV-20, which possesses a higher efficiency than E-3 (PZhV-20 was applied without crushing of cartridges).

During laboratory tests E-3 in cartridges 36 mm in diameter transmitted detonation in the open air only for 3 cm, i.e., close to the least indices of Ammonite No. 8. In the presence of a radial gap charges of E-3 in steel pipes gave attenuation of detonation on 3 and 4 cartridges. However, in the absence of a radial gap this explosive faultlessly transmitted detonation in steel pipes through a sand plug of 4.5 cm, i.e., significantly better than Ammonite No. 8 and close to Pobedite PU-2. We considered that E-3 will detonate well in blast holes with crushing of cartridges.

In the cross-cut of the mine E-3 was tested only in the form of notched and crushed cartridges inserted in blast holes one by one. Ammonite PZhV-20 was tested as whole cartridges inserted in blast holes according to the effective rules of a solid column,and also in two cycles with application of notching and crushing of cartridges. Drilling of blast holes was by electric drill, and since no special measures for their purification were undertaken, they were obstructed by bore meal. The data of these tests are given in Table 6.

Table 6

Results of Mine Tests of Ammonite PZhV-20 and Explosive E-3 in Different Conditions of Loading

1) ВВ и условия заряжания	2) Количество взорванных шпуров	3) Количество случаев неполной детонации
4) Аммонит ПЖВ-20 5) Патроны целые, досылка колонкой	123	5
4) Аммонит ПЖВ-20 6) Патроны раздавливались и досылались по одному	48	0
7) ВВ типа Э-3 6) Патроны раздавливались и досылались по одному	112	0

1) Explosive and condition of loading; 2) Number of detonated blast holes; 3) Number of cases of incomplete detonation; 4) Ammonite PZhV-20; 5) Cartridges whole, inserted as a column; 6) Cartridges crushed and inserted one by one; 7) Explosive E-3.

Thus, Ammonite PZhV-20 with the accepted mining technology of explosive work and thorough fulfillment of/rules gave one incomplete detonation in every 25 detonated blast holes. With the introduction of crushing the same Ammonite gave not one case of incomplete detonation in 48 detonated blast holes. E-3 in 112 detonated blast holes also did not give one case of incomplete detonation, although its detonational ability, determined by standard methodology, is low. Mine tests confirmed the conclusions of laboratory investigations; however they were conducted on a limited scale, and to draw final conclusions from them would be premature.

Main Conclusions

1. One of the main causes of incomplete detonation of blast-hole charges in coal mines is the presence of a radial or lateral gap between cartridges and the walls of the blast hole. Products of explosion, being moved along this gap, lead the detonation front and compact the explosive ahead of it, which can, in the process of explosion, lead to loss of detonation ability of the charge.

2. Harmful influence of radial gap is especially strengthened during its combination with even a small plug of bore meal, which sharply delays transmission of detonation between cartridges and thereby expedites the overcompacting of the explosive by the leading flow of gases. The combination of a radial gap with small plugs (1--2 cm) should be considered the main cause of high frequency of incomplete detonations of not only safety Ammonite, but also Pobedite, in the coal industry.

3. The main directions of the struggle with incomplete detonation of charges in blast holes should be the following:

a) removal of radial gap between lateral surface of cartridges and walls of blast hole, which can at present be realized by the adoption of the known method of notching and crushing of cartridges during their insertion in the blast hole, and in the future by the development and adoption of mechanical methods of loading blast holes;

b) improvement of purification of blast holes of bore meal, since while the removal of the radial gap lowers the harmful influence of plugs, it does not exclude it;

c) improvement of detonation properties of safety explosives, especially with respect to inclination to overcompacting, and support of preservation of explosive quality in the process of transportation, storage and use.

4. The investigations proved the unsoundness of appraising the detonation properties of explosives in blast holes on the basis of results of tests of transmission of detonation in the open air. For correct appraisal it is necessary to use tests of the type described in the article.

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33. Concerning the Question of Factors Determining the Possibility of Burning-out of Explosives in Blast Holes

The question about the causes and possibilities of preventing burning-out of explosive charges in blast holes is at present one of the most pointed problems of providing safety for explosive operations in coal mines.

The appearance of burning of an explosive charge is undesirable for many reasons.

In the first place, it creates the danger of a delayed explosion, since burning for a certain length of time can change into an explosion. A demolition expert, after returning to the site, can be stunned by this explosion. Secondly, during burning will be formed much more poisonous gases (NO and CO), than at detonation, which may cause poisoning of the workers in the mine. In the third place, if instead of an explosion, burning-out occurs, then the explosive does not do the job that it should perform. Fourth: for coal mines especially, burning an explosive is much easier than its explosion, and it ignites a methane-air mixture or coal dust.

During explosive operations, detonation of charges is set off by explosion of the percussion cap-detonator. Burning-out with this can appear only in a case, if at least part of the charge is not detonated.

The main property of an explosive, determining the possibility of failure of explosion, is its detonation ability, the characteristics of which are the critical diameter of detonation and the ability to transmit the latter to a distance.

The possibility of burning-out of the failing charge, naturally, depends on

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the ability of the explosive to burn, which can be characterized, for example, by the critical diameter of burning.

Both shown characteristics can considerably depend on the density of the explosive. Also, for ammonites, including ammonites with small contents of nitro esters, the detonation ability with an increase of density is decreased, the ability to burn, as a rule, increases [1]. Consequently, from the point of view of the possibility of burning-out, an increase of density is doubly undesirable.

Packing an explosive under the conditions of explosive operations can be done in various ways: the substance can be compressed during loading of the blast hole; it can be consolidated also with the gaseous products of detonation, surpassing the detonation wave in the presence of a certain gap between the walls of the blast hole and the charge (channel effect [1]); packing can be done as a result of the action of the shock wave from the explosion of the neighboring blast hole, which is possible in a briefly-delayed explosion, and even with simultaneous damage of a number of blast holes due to the scattering in time of the operation of electrical detonators.

It is obvious that the influence of pressure in a given action should considerably depend on the compressibility, which can be characterized by the dependence of density on the pressure of pressing.

Thus, three main factors determine the possibility of burning-out of a charge in normal conditions of carrying out explosive operations -- the detonation ability of the explosive, its ability to burn and the dependence of these abilities on the changes of the substance possible in explosive operations.

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[1] In light of latest investigations one should note that packing of a charge is not the only factor determining attenuation of detonation as a result of the channel effect.

This investigation was also devoted to determination of the shown dependencies for two industrial explosives on a base of ammonium nitrate — safety ammonite PZhV-20, consisting of ammonium nitrate (64%), trotyl (16%) and sodium chloride (20%), and Pobedit VP-1, containing 9% liquid nitro esters (diglycoldinitrate and nitroglycerine).

Determination of compressibility was done on a mechanical press. A 10g suspension of the explosive was compressed in a glass tube 21.2 mm in diameter by a metallic punch 21.1 mm in diameter, and transferred with constant low speed (25 mm/min). Density was calculated by the curve, recorded by a recording instrument and showing the change of height of the layer of the pressed explosive with pressure.

In Fig. 1 is shown the dependence of density of charge (δ) on the pressure of pressing (p) for both explosives. We see that the compressibility of Pobedit, containing liquid nitro esters and moistening powders, is much higher than ammonite, which does not contain liquid components, even with the absence in it of fibrous additions, which obstruct packing.

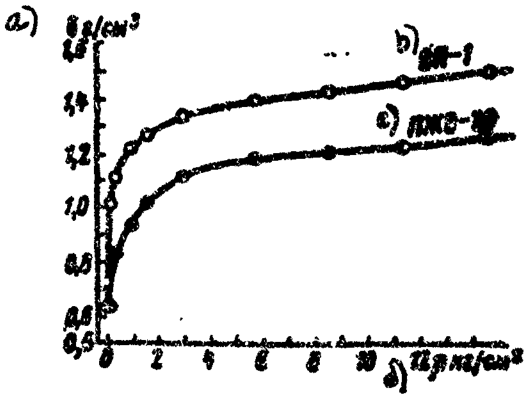

Fig. 1. Dependence of density on pressure of pressing for safety ammonite PZhV-20 and Pobedit VP-1. a) δ g/cm^3; b) VP-1; c) PZhV-20; d) p kg/cm^2;

Determination of the detonation ability was done in two series of experiments. In the first of them an explosive charge was introduced into a paper conical case with a wall thickness of 0.17 mm, length approximately 25 — 30 cm, in one case without packing (average density of PZhV-20 is 1.02 — 1.08 g/cm^3, VP-1, 0.73 — 0.84 g/cm^3) and in the other with packing by a textolite punch manually to the density most attainable with this (for PZhV-20 it was 1.23 — 1.26 g/cm^3, for VP-1 it was 1.48 — 1.54 g/cm^3). Damage of the obtained charges[1] on steel plates showed that in charges of small density the detonation was stopped at near diameters for both explosives (6.5 — 6.7 mm for PZhV-20 and 5.8 — 5.9 mm for VP-1); with tight filling of the paper case, detonation was stopped for PZhV-20 at a diameter of 8.3 — 8.5 mm, for Pobedit — at a much larger diameter (20 — 26 mm)[2].

In order to more accurately determine the dependence of critical diameter of detonation (d_{cd}) on density, the experiments were repeated, and cylindrical telescopic charges were applied in glass tubes, widened on the initiated end. Charges were exploded on brass plates and the passage of the detonation was judged by its imprint.

In Fig. 2 are the results of these experiments. In Fig. 3 they are shown in comparison with data on critical diameter of burning (d_{cb}) [1]. As an argument in Fig. 3 on the axis of abscissas is the pressure of pressing.

We see that main advantage of Pobedit, which is attained by introduction in its composition of sensitizing nitro esters and including an increased detonational ability, is real only in that case, if the possibility of its packing is excluded.

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[1] As the initiator, as in practical conditions, an ED-8-56 electrical detonator mercury fulminate-tetryl was used.

[2] The sample of VP-1, with which the experiments were conducted, was prepared earlier from a sample of PZhV-20, although it was within the limits of a guaranteed period of storage. In order to explain whether the strong dependence of the detonation ability of Pobedit on density is connected with its increased ability to age, the experiments were repeated with samples freshly-prepared in the laboratory. Critical diameter of the detonation was somewhat less, but as before much stronger, than for PZhV-20, and depended on density and especially on the pressure of pressing.

If, however, as this usually occurs under the conditions of practical application, such packing occurs, then the increased compressibility can easily lead to no advantage of Pobedit and it will behave with respect to the possibility of failures and especially burning-out even worse, than the conventional safety ammonites without sensitizers, for example ammonite PZhV-20, the composition of which, incidentally, by no means is impossible to consider rational.

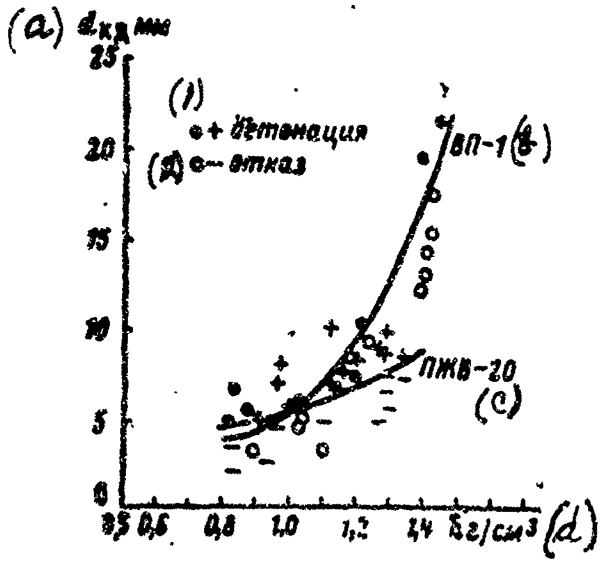

Fig. 2. Dependence of critical diameter of detonation on density for safety ammonite PZhV-20 and Pobedit VP-1.
1) •+ detonation; 2) o- failure.
a) dcd mm; b) VP-1; c) PZhV-20;
d) δ g/cm^3.

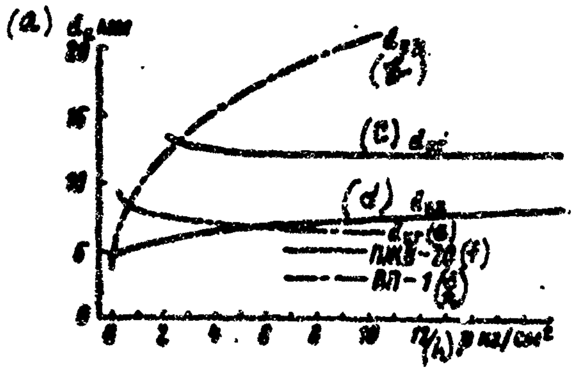

Fig. 3. Dependence of critical diameters of detonation and burning on pressure of pressing for safety ammonite PZhV-20 and Pobedit VP-1.
a) dc mm; b) dcd; c) dcb; d) dcd;
e) dcb; f) PZhV-20; g) VP-1;
h) p kg/cm^2

Curves of Fig. 2 illustrate these relationships. Indeed, only at a filled density (less than 1 g/cm^3) the critical diameter of detonation of Pobedit is somewhat less than for PZhV-20. Upon packing it increases, however, faster than for PZhV-20, and even at a density of 1.2 g/cm^3 becomes greater than the critical diameter of detonation of PZhV-20.

From what has been said, the ways of eliminating the established deficiencies are also clear; here we note two of them: the introduction into Pobedit (in a sufficient quantity corresponding to liquid content) of substances which obstruct packing and the replacement of liquid sensitizers with solid ones [2].

Literature

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2. K. K. Andreyev, V. Z. Smolyanitskiy and N. S. Bakharevich. Author's Certificate No 1894/351529 with priority dated 6 February 1947. L. Médard, Mem. des poudres, 1950, 32, 219.

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Chapter 3 Article 34

Pages 499-514

A. I. Gol'binder

34. Self-ignition of Liquid Explosive Mixtures

Investigations of self-ignition (flash) of explosives are conducted, as a rule, with individual explosive compounds [4]. In the given work certain results of investigation of flash of liquid explosive mixtures are presented.

Ignition of systems of such a type is usually studied in reference to conditions of burning in liquid-fuel rocket engines, where corresponding liquids are mixed and are ignited in the form of the smallest drops [1], [11], [13]. In our work we investigated the self-ignition of mixtures in the form of compact liquid charges [1]. Besides the interest that such an investigation presents for the solution of certain applied problems, it allows also to expand presentations on the mechanism of self-ignition of explosives in general.

Experimental Part

Self-ignition of Liquid Mixtures of Tetranitromethane With Organic Amines

As is known [11], during the mixing in the usual conditions of tetranitromethane with many liquid organic amines self-ignition occurs. We studied this phenomenon for five amines: aniline, o-toluidine, extraline (mixture of aniline, mono- and dimethyl aniline), xylidine (technical mixture of isomers) and triethylamine. We investigated in the most detail mixtures with aniline, for which the delay of self-ignition at room temperature constitutes several tens of seconds.

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[1] A significant part of the experiments were carried out in the All-Union Scientific Research Institute of Drilling Technology with the participation of S. A. Lovl', N. I. Kozlova, and G. V. Dims, to whom the author expresses sincere gratitude.

As was shown by special experiments, whose description we omit for brevity, the time of mutual dissolution of components of a given mixture in the usual conditions of our experiments (pouring of tetranitromethane into a vessel with aniline) constitutes only an insignificant fraction of the induction period.

In part of the experiments the delay of self-ignition was determined with the help of an inductometer with a photocell, whose diagram is shown in Fig. 1. A definite quantity of amine was placed in a crucible fixed in the instrument so that the beam of light from the illuminator passed above level of liquid and struck the photocell. During pouring of tetranitromethane into the crucible, the stream crossed the beam of light and by decreasing the illumination of the photocell caused a change in the photocurrent registered on the oscillogram. The moment of ignition was fixed on the same oscillogram by the jump in the photocurrent, caused by the glow of the flame. In another part of the experiments, when the induction period was comparatively great, the delay time was determined by visual observation with a stop watch.

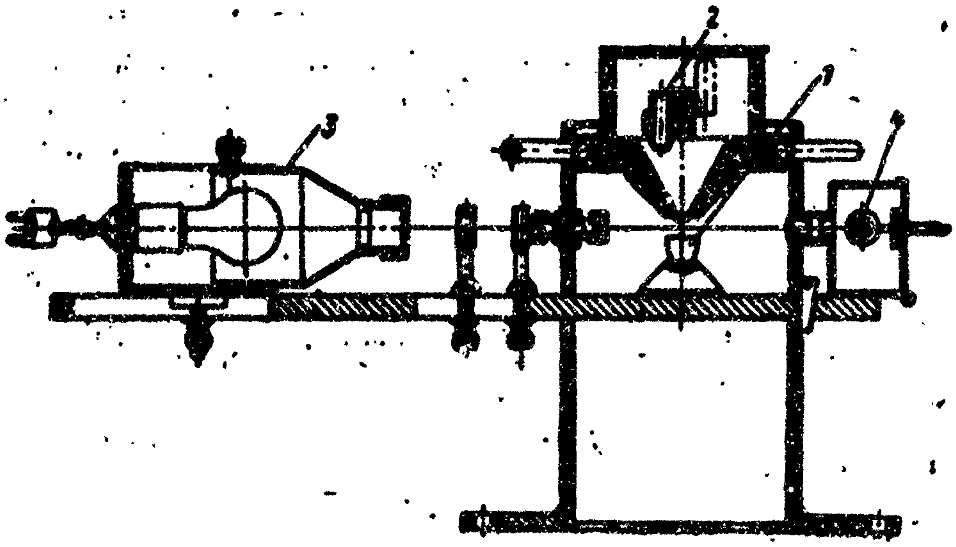

Fig. 1. Diagram of inductometer.

1) crucible with fuel; 2) test-tube with oxidizer;
3) illuminator; 4) photocell.

The delay of self-ignition depends on the concentration of components in the composition of the mixture. The character of this dependence is seen in Fig. 2, where results are presented of experiments with a mixture of tetranitromethane and aniline at 15—17°; the general volume of mixture remained constant at 3.5 ml. As can be seen from the graph, in the area of mixtures with a negative oxygen balance, the induction period changes comparatively weakly with composition. Analogous results were obtained in experiments with xylidine and o-toluidine.

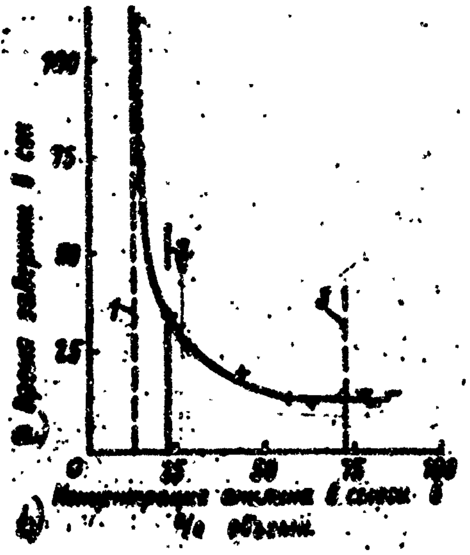

Fig. 2. Dependence on composition of delay of self-ignition of mixture of tetranitromethane and aniline.

1)Lower and 3)upper concentration limits of self-ignition; 2)stoichiometric composition; + —ignition; — —flameless decomposition.

a) Delay time in sec; b) concentration of aniline in mixture in vol %.

In connection with this, in the majority subsequent experiments we worked with mixtures having a certain surplus of fuel against stoichiometry, and for different amines applied constant volumes of fuel (1 ml.) and oxidiser (2.5 ml.). Thus we assured constancy of conditions of mixing, which in the given interval of concentrations have a stronger influence on delay time than small oscillations of molecular composition. The results of experiments conducted in the described conditions with 4 amines are presented in Table 1.

Table 1

Delay of self-ignition of binary mixtures of tetranitromethane (2.5 ml.) with amines (1 ml.)

1) Амин	Количество опытов 2)	Время задержки сек. 3)	Температура опыта °C 4)
5) Анилин	10	36±9	16
6) о-Толуидин	12	7,8±3,5	24
7) Ксилидин	22	1,1±0,4	22
8) Триэтиламин	15	0,42±0,04	20

1) Amine; 2) Number of experiments; 3) Delay time, sec; 4) Temperature of experiment, °C; 5) Aniline; 6) o-toluidine; 7) Xylidine; 8) Triethylamine.

From investigation of the flash of the usual explosives we know the influence of the mass of the heated substance on the minimum temperature of self-ignition. Small samples are decomposed without ignition at temperatures, at which large ones are ignited. Usually such phenomena are explained, solely on the basis of thermal presentation, by the fact that with an increase in the sample the speed of heat emission, proportional to the volume of substance, grows faster than the speed of heat loss, proportional to its surface.

We observed an influence of mass for the spontaneously inflammable mixtures considered here. In definite conditions, ignition of a mixture of aniline and tetranitromethane of constant composition occurred only in that case, when its general quantity exceeded 1.2 ml. In other experiments, also with constant composition of the mixture, we noted a small reduction in the delay time with an increase in the general mass of the liquid explosive.

It would have been possible to think that in a given case the influence of mass would be stipulated only by the relative change in the speed of heat emission and heat loss with a change in the quantity of mixture. Experiments with mixtures of aniline and tetranitromethane showed, however that thermal processes alone cannot explain the mechanism of the considered phenomenon. We will list the following characteristic data from this series of experiments.

Equal quantities of mixture at a constant relationship of the volumes of fuel and oxidizer (1 : 2.5) were obtained in two vessels of identical dimensions. One of the vessels was glass and was located during the experiment in air, and the other was of steel and was located in energetically stirred water at the same temperature. In spite of essential distinctions in the conditions of heat loss, the minimum quantity of mixture with which at least in one of five parallel experiments self-ignition appears, and also the duration of the induction period, were identical in both vessels.

The minimum height of the layer of mixture with which ignition is still possible is practically constant. Thus, in aluminum flasks with diameters of 8 to 28 mm, at room temperature, the minimum height of layer of mixture with which ignition still appears, was identical and equal to 2 mm[1]. Thus the minimum volume of liquid mixture with which self-ignition is still observed a constant initial temperature increases with the square of the diameter.

Further, we prepared 1.2 ml, of the mixture in glass vessels whose form and dimensions are shown in Fig. 3. With this there were no ignitions in open vessel 2, but in semiclosed vessel 1 they appeared regularly.With a change in subsequent experiments of the magnitude of the charge it was shown that in the semiclosed vessels the minimum quantity of mixture with which ignition still appears is, other conditions being equal, 2—4 times less than in open vessels. Thus, here was observed an essential distinction in the conditions for the appearance of flash with very close conditions of heat loss.

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[1] In the absence of self-ignition, at a short time after mixing of the components flameless decomposition appears; the mixture seems to boil, there is stormy emanation of gas, part of the liquid is atomized, and the remainder obtains a tarry consistency.

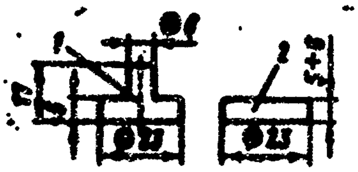

Fig. 3. Glass vessels for experiments on self-ignition of a mixture of tetranitromethane and aniline.

1) semiclosed; 2) open.

To study thermal phenomena in the course of the induction period, in subsequent experiments on the inductometer shown in Fig. 1 we introduced into the crucible the junction of a low-inertia thermocouple. In some of a series of parallel experiments the thermocouple junction was placed near from bottom of the crucible, so that after the pouring of the oxidizer it was in the liquid. In other experiments the junction was at a height of 3—7 mm above the level of the liquid mixture in the crucible. Changes in the emf in the given case were recorded through an amplifier on the same oscillogram as was used for changes in the photocurrent. One such oscillogram is shown in Fig. 4.

In the process of investigation it was desirable to register changes in the temperature in the liquid and in the vapor over it in one and the same experiment. In connection with the fact that in our setup there was only one amplifier of thermal emf, some of the parallel experiments were conducted with differential thermocouples, one junction of which was placed in liquid mixture, and the other —above it.

As a result of a large number of experiments it was established that for the entire induction period, the temperature of the liquid remains practically constant and equal to the initial temperature of the components of the mixture. A practically cold mixture is ignited and then burns. Just before the actual ignition, and sometimes even after it, the thermocouple located in the liquid starts to mark a weak and relatively slow warm-up. With the studied amines, the maximum

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warm-up to the moment of appearance of flame marked by the thermocouple whose junction was located in the liquid did not exceed 15°, and in the majority of the experiments was less than 10°.

Fast warm-up of gases or vapor over the liquid precedes ignition in all cases. In the gas phase the rise of temperature occurred with a speed of the order of many hundreds of degrees per second. Our system of recording was too inertial and therefore the maximum temperature registered by it up to the moment of appearance of flame did not exceed several tens of degrees. In all experiments with differential thermocouples, before ignition we noted a fast relative warm-up of the junction located above the liquid.

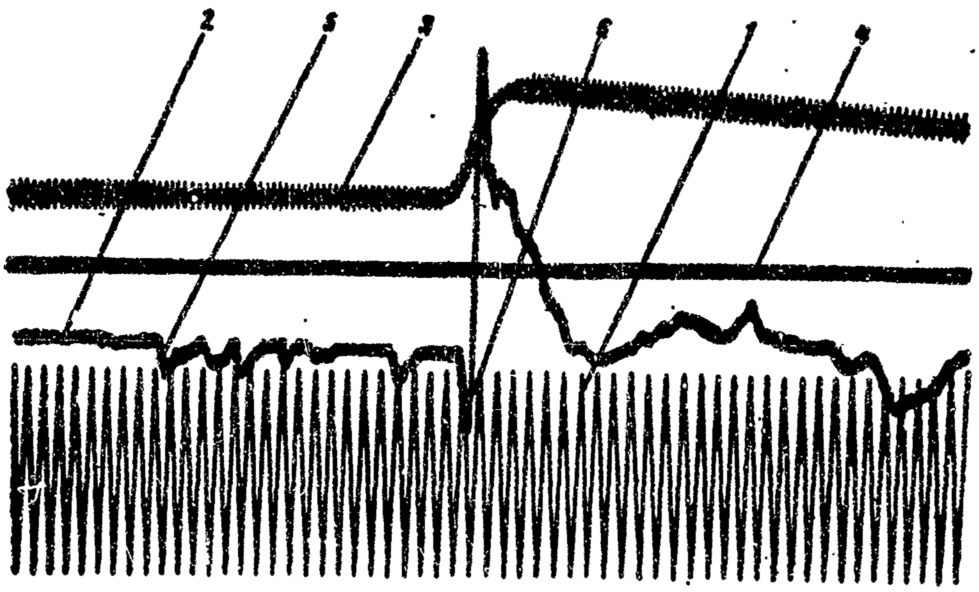

Fig. 4. Sample of oscillogram during investigation of self-ignition of liquid explosive mixtures.

1) time scale (curve of standard frequency); 2) curve of change of photocurrent; 3) curve of change in thermal-emf; 4) zero line; 5) moment of pouring of oxidizer, 6) moment of appearance of flame.

We will note one more important observation: for all investigated mixtures self-ignition is preceded by "boiling", during which emanating gases or vapors seize extremely small drops of liquid. Above the liquid there appears a unique kind of "smoke". This phenomenon is clearly established on the oscillograms by the decrease in photocurrent before ignition and is easily observed visually in cases of mixtures with a large delay times, but in those with small delay, by high-speed filming. Intense gas generation starts, as a rule, in the very end of the induction period.

It was assumed that the main process proceeding during a significant part of the induction period is a thermoneutral or weakly exothermal reaction of the amine with the oxidizer, leading to the formation of a condensed, comparatively stable intermediate product. Subsequent stages of the process will proceed with a speed sufficient for self-ignition only when the concentration of this intermediate product attains a certain limit. This assumption was confirmed by the following simple experiments.

1. At constant conditions we prepared 3.5 ml of mixture by two methods: at first we poured in the vessel a small part of the components [1] (0.32 ml. of aniline and 0.8 ml. tetranitromethane), and after a certain time (called in the future the hold time), the remainder.

With an increase in the hold time to a certain limit, the delay of self-ignition, counted from moment of pouring of the main mass of the mixture, was noticeably reduced. Results of these experiments are presented in Table 2.

Analogous experiments with different relationships of the volumes of the first and second portions of the mixture showed that the delay of self-ignition at identical hold times is reduced more, the greater is the first portion, i.e. the, higher is the concentration of intermediate products in the mixture.

2. To a significant volume of amine (20—50 ml.), during energetic stirring, we introduced by drops a small quantity tetranitromethane (0.04—0.10 moles per

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[1] In the given conditions such a small quantity of mixture is incapable of self-ignition.

Table 2

Reduction in delay of self-ignition as a result of preliminary storage of intermediate products

Время выдержки сек. 1)	Среднее время задержки самовоспламенения в сек. 2)	Время выдержки сек. 1)	Среднее время задержки самовоспламенения в сек. 2)
0	61	40	35
10	53	60	22
20	42	90	20

1) Hold time, sec; 2) Average delay time of self-ignition in sec.

mole of amine). As a result of the reaction occurring blackening of the amine was observed. With such blackened amine we conducted further experiments on self-ignition at the usual relationship of volumes of fuel and oxidizer (1 : 2.5).

The results of the experiments are presented in Table 3. As can be seen from this table, in a mixture containing a surplus of amine, the intermediate product is fully stable.

For explosive chemical compounds the fact has long been established that here is a decrease of delay of flash with a growth of temperature. An analogous phenomenon is observed for spontaneously inflammable liquid mixtures. To judge the character of this dependence in the last case with sufficient accuracy is difficult, since we could investigate on the example of mixtures of tetranitromethane with anilines only in a very narrow interval of temperatures. Below 14° tetranitromethane hardens, while temperatures higher than 60° the delay of self-ignition is reduced so much that the time of mixing of components in our instrument constitutes a significant part of it.

If we consider that the dependence of delay time of self-ignition on temperature has in the given case the same form as that for other studied systems, then effective activation energy is about 12 kcal/mole.

Table 3

Change of delay of self-ignition with addition of intermediate products

Название амина 1)	Введено тетранитрометана в мл на 100 мл амина 2)	Задержка самовоспламенения в сек. 3)	Промежуток времени от приготовления раствора промежуточных продуктов до определения задержки самовоспламенения 4)
5) Анилин	7) нет	32±3	—
"	10	11±2	До 60 мин. 9)
"	7	9±1	До 60 мин. 9)
"	7	10±1	12 суток 8)
6) о-толуидин	7) нет	49±5	—
6) о-толуидин	5	8±1	До 60 мин. 9)
6) о-толуидин	5	9±1	10 суток 8)

1) Name of amine; 2) Tetranitromethane introduced, in ml per 100 ml of amine; 3) Delay of self-ignition in sec; 4) Interval of time from preparation of solution of intermediate products to determination of delay of self-ignition; 5) Aniline; 6) o-toluidine; 7) None; 8) days; 9) To 60 min.

A series of experiments with a mixture of tetranitromethane and aniline was conducted at various compositions of the atmosphere over the liquid. It was found that, other conditions being equal, the average delay time of self-ignition in atmospheres of air, nitrogen, and carbon dioxide constituted 43^{+7}_{-13}, 49^{+6}_{-14} and 42^{+13}_{-11} sec, respectively.

Self-ignition of Liquid Mixtures Based on Concentrated Nitric Acid

We studied, by the methodology described in the preceding section, self-ignition appearing during the mixing of concentrated nitric acid with certain amines (aniline, toluidine, xylidine), phenols (resorcin, pyrocatechin) and unsaturated compounds (solutions of divinylacetylene in xylene, styrene in gasoline, trivinylglycerine, etc.). Almost all the investigated mixtures are self-igniting at ordinary temperatures, with delay measured in fractions of a second. In such systems delay time is determined in significant measure by conditions of mixing of components [11], [14], [15], [17]. We will stop briefly on the main general regularities established for self-ignition of different fuels with nitric acid.

Just as for mixtures with tetranitromethane, a strongly exothermal reaction, leading to self-ignition also in the case of nitric acid appears in the gas phase. This is confirmed both by our recordings of thermal emf with different locations of thermocouple junctions and by data of high-speed filming and other investigations [11], [14].

In contrast to that which was observed for mixtures based on tetranitromethane, from the moment of mixing of concentrated nitric acid and a reactive fuel there appears in the condensed phase an exothermal reaction and the temperature of liquid rises rapidly.

During the short induction period a thermocouple located in the liquid shows an approximately constant temperature of 80 to 130°, depending upon the type of fuel and the composition of the mixture. With this there occurs not only gas formation, due to the flow of the chemical reaction between the fuel and the oxidizer, but also boiling. It is this boiling which limits, apparently, the maximum temperature of the liquid, which remains approximately the same after ignition up to the moment when the flame front approaches the junction of the thermocouple. Thus, in the case of mixtures with nitric acid the explosive which is ignited and burns is heated to the boiling point by the heat of the primary stages of the reaction.

Flash of Liquid Explosive Mixtures of Tetranitromethane With Organic Fuels During Heating

Tetranitromethane well dissolves different organic liquids and with many from them will form solutions, which are stable, at least in small quantities, at ordinary temperatures.

Many of the experiments on the flash of liquid explosive mixtures during heating were conducted in the following conditions. A massive brass block was heated with the help of an electric furnace. In the block we drilled 4 sockets 20 mm in diameter, filled with Wood alloy. In one of the sockets we embedded a thermometer, and in the remaining ones we placed glass test-tubes 15—17 mm in diameter submerged in the alloy to half their length. After we established the given temperature for each experiment, we introduced into the test-tube by pipette about 0.1 g (0.06—0.08 ml.) of the investigated mixture. In the experiments we established the presence or absence of flash, its character, and the interval of time from the introduction of the liquid into the test-tube to flash.

The mixtures we tested are highly volatile substances, and therefore in small quantities they gave flash only at a relatively high temperature. At lower temperatures there occurs only fast evaporation of the mixture, sometimes with noticeable decomposition. Not one of the mixtures studied flashed in these conditions at a temperature lower than 160°

For the same reason (fast evaporation of a small sample) we did not observe flash with a delay of more than 10 sec. If in this time flash did not occur, then it could not appear subsequently, since the small quantity of mixture had been volatized.

In Table 4 are presented results of the investigation of 18 binary mixtures of tetranitromethane with different liquid fuels. We conditionally called the minimum temperature of metallic block at which ignition occurred with a delay of not more than 5 sec. "temperature of flash". In this table are given for certain mixtures the temperatures of "beginning of boiling", determined by the method of M. N. Sivclobov /18/, and the value of the mass burning rate at this temperature, calculated by extrapolation of data obtained in the range 20—70°. For all mixtures compositions near to zero oxygen balance were tested.

With an increase in the quantity of heated substance, the temperature of flash is lowered noticeably. Thus, in a quantity of about 0.1 ml, a mixture of

Table 4

Temperature and character of flash of binary mixtures based on tetranitromethane

(Conditional designations in column "Character of flash": 1—soundless ignition; 2—flash with whistling sound; 3—flash with "clap"; 4—flahs with strong "clap"; 5—explosion with splitting of test-tube)

1) Наименование горючего	2) Температура вспышки °C	Температура начала кипения смеси 3) °C	Массовая скорость горения при температуре начала кипения 4) г/см^{2}сек	5) Характер вспышки
6) Бензольная головка	180	—	0,3	4
7) Стирол	230—270	112	0,3	4 и 5
8) Фурфурол	240	122	0,25	5
9) Тривинилглицерин	278	—	—	3
10) Керосин тракторный	285	123	—	3
11) Бензальдегид	280	113	—	4
12) Бензин Б-70	290	—	—	3
13) Соляровое масло	300	117	—	2 и 3
14) Этанол	300	90	0,14	3
15) Автол	310	125	—	3
16) Фракция бензина Б-70, выкипающая до 100°	325	90	—	5
17) Ксилол (смесь изомеров)	340	—	—	3 и 4
18) Грозненский бензин прямой гонки	370	114	0,15	4
19) Мононитрометан	435	—	—	1
20) Толуол	500	140	0,08	2
21) Нитробензол	510	129	0,16	3
22) Дихлорэтан	510	120	0,07	1
23) Бензол	520	104	0,15	2

1) Designation of fuel; 2) Temperature of flash, °C; 3) Temperature of beginning of boiling of mixture, °C; 4) Mass burning rate at temperature of beginning of boiling, g/cm^2 sec; 5) Character of flash; 6) Benzene head; 7) Styrene; 8) Furfurole; 9) Trivinylglycerine; 10) Tractor kerosene; 11) Benzaldehyde; 12) Gasoline B-70; 13) Solar oil; 14) Ethanol; 15) Lubricating oil; 16) Fraction of gasoline B-70, boiling away up to 100°; 17) Xylene (mixture of isomers); 18) Grozny gasoline, straight-run; 19) Mononitromethane; 20) Toluene; 21) Nitrobenzene; 22) Dichlorethane; 23) Benzene.

tetranitromethane and benzene flashes only at a stove temperature higher than 500°. During boiling of 25 ml of a mixture of the same composition (temperature of liquid not higher than 130°) through 3—5 min we observed flash, in the majority

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experiments ending in explosion. The connection of temperature of flash and mass of heated substance was clearly noticeably also on the example of a mixture of tetranitromethane with a light fraction of pyrolysis of oil, the so-called benzene head, containing significant quantities of unsaturated hydrocarbons. Such a mixture of a composition near to zero oxygen balance, taken for experiments in a quantity of 0.05 ml, ignited at 190°; the same mixture in a quantity a little exceeding 1 ml, is self-ignited at 40—45°; if we prepare simultaneously more than 20 ml of this mixture, then its ignition sets in already at 15—18°.

We conducted a further series of experiments with trinary mixtures. As oxidizer in them we applied, as before, tetranitromethane, but as the fuel —a mixture of benzene and styrene. The relationship of fuel and oxidizer in all experiments was maintained near to zero oxygen balance, but we changed the composition of the fuel from experiment to experiment, increasing the content of styrene.

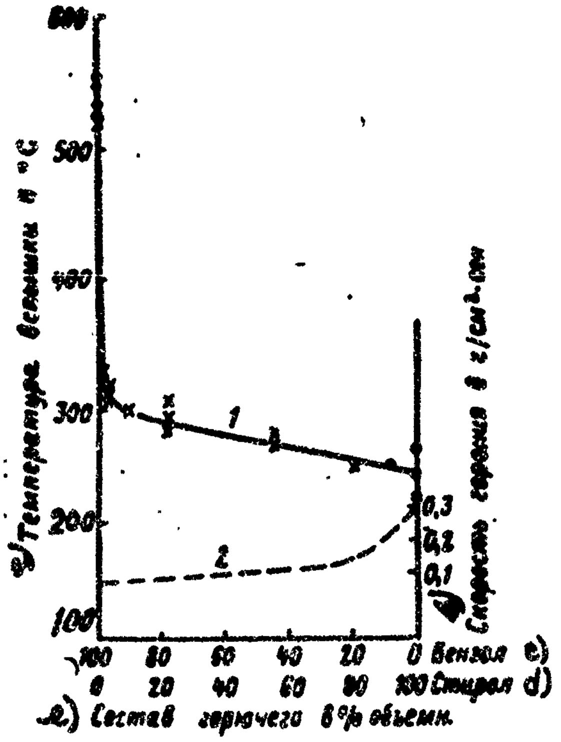

Fig. 5. Dependence of temperature of flash and burning rate of the trinary mixture tetranitromethane—benezene —styrene on the composition of the fuel.
1—temperature of flash, 2—burning rate (points show experiments in which flash had the character of explosion).
a) Temperature of flash in °C; b) Burning rate in g/cm² sec; c) Benzene; d) Styrene; e) Composition of fuel in vol %.

Results of the experiments are presented in Fig. 5. From the graph it is clear that the introduction into the composition of the fuel of a very small quantity of styrene (0.7—1.0 vol %) causes lowering of temperature of flash by approximately 200°; a further increase in the content of styrene causes only a relatively slow fall. With an increase in the content of styrene in the fuel the burning rate also grows, first slowly and then faster; simultaneously the intensity of flash is strengthened. Analogous results were obtained in experiments with a trinary mixture of tetranitromethane—benzene—fraction of gasoline of pyrolysis (benzene head).

For binary mixtures of tetranitromethane with furfurole, mononitrobenzene, mononitromethane, or xylene we investigated the dependence of flash temperature on the relationship of the quantities of fuel and oxidizer in the composition of the mixture. The biggest distinction in flash temperature was observed in the system tetranitromethane—mononitromethane, where at a zero oxygen balance flash appears at 435°, but in a mixture with a large surplus of oxidizer—at 330°. For other mixtures the change in the flash temperature with composition did not exceed 30° for all intervals of concentration studied (oxygen balance from minus 40 to plus 30). In all studied mixtures the minimum of the curve "flash temperature—composition" appeared in the same region of concentrations as the maximum of the curve "burning rate—composition".

Discussion of Results

Let us consider first the results obtained during the study of self-ignition of mixtures of tetranitromethane and amine. It was experimentally established that up to the moment of ignition, warm-up in the condensed phase is very small. Even after ignition, the temperature of the liquid, up to the moment when the front of burning approaches the junction of the thermocouple, remains near to the initial temperature of the components of the mixture. The experimentally measured "pre-explosion warm-up" of the liquid was less than that calculated by

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the theory of thermal ignition [12] for the case of conductive heat transfer and was known to be less than that during convective heat exchange in a liquid stirred by bubbles of formed gases. This circumstance alone speaks of the fact that in the given case it is impossible to consider that self-ignition appears because of thermal self-acceleration of the process, as it proceeds in the condensed phase.

Other data confirm this point of view. First of all it is necessary to note the results of direct measurements of temperature in the liquid and in the gas phase over it, showing that a fast warm-up, preceding self-ignition, appears in the gas phase. The buildup of temperature of the gas-vapor mixture directly before flash proceeds at a very great speed, as one would expect from the theory for thermal self-ignition in the gas phase [12]. Curves, obtained during measurement of the temperature of the liquid are considerably distinguished from those obtained for gas, not only in magnitude of maximum warm-up before ignition or the position of beginning of temperature rise relative to the moment of appearance of flame, but also by the character of the curve "temperature--time". In the liquid the temperature rise during the entire time preceding ignition, and even for a certain time after it, occurs significantly slower than in the gas.

Very indicative also are the results of experiments in the two types of vessels shown in Fig. 3. The conditions of heat exchange of liquid with the environment in both vessels are identical, but the critical conditions of self-ignition in them are considerably different. These distinctions are caused by the peculiarities of the flow of the reactions in gas phase, completed by flash.

With identity of the conditions of heat dissipation from the reacting gas the speed of the reaction leading to ignition and, consequently, the critical conditions of its appearance, should be determined by the concentration of reactive gases. In the considered experiments this concentration depended on the relationship between the speed of entering of corresponding gases (or vapors) from the liquid and the speed of their dilution by ambient air. In the simplest assumptions the quality of gases, emanating in a unit of time per unit of surface of liquid (specific speed of gas formation) should be proportional to the height of the liquid layer. Near to the critical conditions this concentration was insufficient for ignition in an open vessel of small height, where there occurs fast dilution of the reactive gases (or vapors) as a result of mixing with ambient air. In a semiclosed vessel the conditions for the formation of a gaseous (or vapor or gas drops) mixture of the necessary concentration are favorable.

In an open cylindrical vessel of constant diameter, with an increase in the volume of the prepared mixture, and, correspondingly, the height of its layer, the specific speed of gas formation increases. Starting with a certain critical height of the liquid layer, this speed becomes sufficiently great so that, in spite of dilution of emanating gases or vapor by ambient air, the concentration of them necessary for self-ignition could be created.

At first glance the proposals on the appearance of flash in the gas phase contradict the results of experiments conducted in atmospheres of air, oxygen, and carbon dioxide, where we observed practically identical delay. Actually there is no contradiction here. Delay of self-ignition, constituting for a mixture of tetranitromethane and aniline tens of seconds, is the sum of time of flow of at least two different macroscopic stages of the process. The first of them proceeds in the condensed phase and its duration depends on the time of accumulation of active intermediate products and the development of chemical self-acceleration of the process leading to the formation of gases. The second stage is determined by the time for the creation of the necessary concentration of reactive substances in the gas phase and the thermal self-acceleration of the reaction proceeding here to flash. The composition of the gas medium, obviously, can influence only the second stage of the process. The interval of time from the beginning of gas liberation to the appearance of flame constitutes, as the experiments show, only an insignificant fraction of the total delay time. It is clear that even an essential change of this fractions in connection with a change in the composition of the atmosphere, is not reflected in a noticeable form in the experimentally determined delay. Additionally one should note that the experiments in atmospheres of different gases were conducted under conditions far from the critical parameters of self-ignition. It is possible to consider that, for example with a lesser height of the liquid mixture layer the influence of the composition of the atmosphere would be more strongly developed.

Interesting conclusions can be drawn from the results of experiments carried out in various conditions of heat loss. The fact that there is practically no change in the delay time of ignition with a change in heat loss could be explained, analogously to the preceding, by the significant predomination of the time of isothermal chemical self-acceleration over the duration of thermal self-acceleration.

The experiments established, however, that not only delay, but also the critical conditions of ignition (in the given case, the minimum mass of liquid explosive) remain constant with a change in the conditions of heat loss. This confirms the proposed mechanism, according to which thermal self-acceleration (thermal explosion) occurs in gases, vapor, or droplet suspensions over the liquid. Let us remember that in some of the experiments of this series we applied glass vessels surrounded by air, and in others--steel ones of like dimensions located in water. As calculation shows, the coefficient of heat-transfer from liquid inside the vessel to the environment changes by at least several tens of times, while for a gas inside the vessel, this coefficient is increased with such change of conditions by no more than one and a half to two times. If a decisive role is played by thermal explosion in the condensed phase, then as calculation shows, the critical dimension of the charge should change considerably with transition from a glass to a steel vessel. This was not observed in the experiments.

In the case when into the mixture, by one or another method we introduce previously prepared intermediate products of the interaction of tetranitromethane and aniline, the delay time of self-ignition is sharply reduced (see experiments in Tables 2 and 3). This shows that the main part of the induction period is occupied by reactions in the condensed phase leading to the formation of active intermediate products. Ascertaining the mechanism and kinetics of these reactions was the object of a special investigation. Here we will limit ourselves to only indications that toward the end of the induction period free amine is practically absent in the mixture. The self-accelerated interaction of products of the primary reaction with tetranitromethane leads later to the formation of gases (vapors), which ignite when their concentration attains a certain limit.

The self-ignition of liquid explosive mixtures containing nitric acid as oxidizer also appears in the gas phase. However in the course of the preignition processes a clear distinction is observed. In the case of mixtures with nitric acid the processes proceeding in the condensed phase are strongly exothermic, in consequence of which the liquid is intensely heated. The content in the mixture of comparatively highly volatile components naturally limits the maximum warm-up of the liquid, by the boiling point. In connection with this, in gas-phase reactions leading to self-ignition, side by side with the intermediate products formed in the liquid phase, the vapors of the parent substances of the products of their decomposition can participate also. While in the case of mixtures of tetranitromethane with amine the cold liquid was ignited and subsequently burned, the ignition and burning of mixtures with nitric acid occurs when the liquid is heated to boiling [1].

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[1] Phenomena proceeding in the process of burning will not be examined here. We will note only one circumstance, essential both for ignition and for the subsequent burning of an explosive liquid. Tetranitromethane readily dissolves liquid organic fuels. In connection with this, during significant delays of self-ignition there will always be formed a homogeneous solution. Nitric acid and the majority of liquid fuels do not possess mutual solubility. Besides, the delay of self-ignition for mixtures with nitric acid is very small, therefore to its beginning, as a rule, a uniform solution is not obtained; there is ignited and burned in this case a suspension of drops of one component in another. The dimensions of drops, and consequently, of the surface of contact between reacting substances, depends thus on the physicochemical properties of both miscible liquids and also on the conditions of their mixing. In many cases it is the influence of the last factor which determines the delay time of self-ignition and the state of the burning mixture.

The self-ignition of liquid explosive mixtures at an increased temperature, obtained by means of heating them from an external source (thermal ignition), has much in common with the flash of ordinary explosives. We will note from this point of view the clear connection between the intensity of flash and the speed and character of burning, which was established for individual explosives by K. K. Andreyev [3]. As we have seen, the sharpest, most explosive character belongs to the flash of mixtures tetranitromethane with benzene head, styrene, and furfurole. These mixtures burn with comparatively great speed, their burning is unstable and even at ordinary temperatures in glass pipes 5--7 mm in diameter cases were observed of transition of burning to explosion. At increased temperatures, obtainable in liquid at the moment of thermal flash, the stability of burning is still less and even in small quantities the mixtures investigated flash with great intensity.

For certain individual explosives the phenomenon of an "upper limit" of flash temperature was detected [2]. This phenomenon is observed for substances having comparatively low boiling points under conditions when the time of chemical self-acceleration of reactions of disintegration is larger than the time of evaporation. The investigated liquid mixtures are volatile; therefore for many of them--for example, for mixtures with benzene, toluene, dichlorethane--under the experimental conditions with small quantities of liquid, the phenomenon of "upper limit" is observed in all temperature ranges from room temperature to about five hundred degrees, when it is already correct to talk not about flash of explosive in the usual meaning, but about the igniting of its vapors by a heated surface. If we increase the mass of explosive, then with the same conditions of heating the time of evaporation grows and self-acceleration of disintegration can occur before all the substance is evaporated. The upper limit of flash temperature can thus be lowered, as was observed in experiments with mixtures of tetranitromethane with benzene, etc.

A graphic presentation of the relative role in the flash process of chemical self-acceleration and the evaporation of substance during heating is given by the results of experiments with the trinary mixture tetranitromethane —benzene— styrene. A mixture of tetranitromethane and benzene is easily evaporated, but in chemical relationship is comparatively inert. Correspondingly, self-ignition of this mixture appears only with a heater temperature at which the mixture of vapors flashes. The temperature of ignition of a mixture of the pure vapors is comparatively high --in the given case, about 500°. After addition to the binary mixture of a small quantity (about 0.5 vol %) of styrene, the condition of evaporation of a drop of the mixture could not be changed considerably. The sharp lowering of flash temperature of the trinary mixture is explained by the fact that the presence in the system of reactive styrene stipulates, at lower heater temperature, the flow with sufficient speed of the processes of formation of active products, so that the concentration of them necessary for self-ignition is created in less time than is required for full evaporation.

If the components of a mixture have different vapor pressures, then, as is known, the composition of the vapor phase can be distinguished from that of the liquid. As is known [7], [8], during the burning of liquid mixtures of highly volatile substances this circumstance causes original phenomena of fractional burnout, caused by difference in the compositions of the liquid and of the vapor over it, and also their changes in the course of propagation of burning. Fractional evaporation plays a definite role also during thermal flash of mixtures; this is evident, for example, in the results of experiments with mixtures of the same components at various relationships between them. In these experiments we established the coincidence of regions of concentrations in which the maximum of burning rate and minimum of flash temperature are observed. During experiments on thermal self-ignition, carried out with very small quantities of the liquid mixture, the influence of fractional evaporation is relatively small. A drop of the mixture, for the most part, can be evaporated in a time less than the delay of self-ignition. Differences in the compositions of liquid and vapor, stipulated by differences in the tensions of vapors of the components, are smoothed in this case.

Comparatively long ago A. F. Belyayev [5] indicated that flash of flying volatile explosives appears in the vapor phase, This position in essence no one now doubts; however until now there was no direct experimental confirmation of it. In works on the theory of thermal explosion of explosives, including some carried out recently [9], [10], [16], this essential circumstance acutally is not considered. During the investigation of liquid mixtures direct experimental confirmation that self-ignition appears in gas phase was obtained.

For the mixtures studied in the given work two different methods of self-ignition were observed.

1. In the condensed phase there proceeds, without essential warm-up of the substance, a self-accelerated process of its transformation to reactive gases. When the concentration of the latter exceeds a certain maximum, the reactions between them are completed by thermal self-acceleration (thermal explosion), leading to flash. The temperature of the condensed substance ignited by this method can be significant lower than its boiling temperature. In connection with this the vapors of the parent substance cannot play an essential role in gas-phase reactions completed by flash.

2. In the condensed phase exothermal reactions will proceed. As a result of chemical and thermal self-acceleration of these reactions there appears progressive self-warm-up. The maximum temperature, however, is limited by the boiling point of the actual explosive or of the products of the primary stages of its transformation [1]. Thermal explosion and ignition occur, as in the preceding case, in the

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[1] Such a role, like boiling, can in certain cases be played by the endothermic decomposition of the parent substance or an intermediate product.

gas phase, but now the vapors of the explosive can participate in them side by side with the products of the primary reactions.

Mechanisms of self-ignition of mixtures and individual explosives should have much in common. It is possible, therefore, to expect that the two methods of self-ignition described will be observed also for certain explosive compounds.

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Chapter 3 Article 35

Pages 515-527

B. N. Kondrikov

35. Intensity of Flash in Explosive Substances

The ability for self-ignition during increased temperature is one of the most common properties of all explosive systems and, in particular, condensed explosives. The main characteristics of self-ignition -- the condition with which it becomes possible (so-called critical conditions) and the dependence of the induction period (delay of flash) on temperature -- were studied by many investigators and, for a number of explosive substances, are quite well known. However these characteristics in essence describe only the development of preparatory, before flame reactions, not at all concerning how the process develops after appearance of flame. Serving as a known characteristic of propagation of flame at flash can be the intensity of the latter, determined by speed of gas formation and increase of pressure during self-ignition. Unfortunately, in the majority of works this side of the question is hardly touched upon. In the best case only the character of the flash is noted, estimated by the force of the sound or by the fact that the glass vessel in which it occurs is split or remains whole during flash.

The problem of this work has been, by using the simplest method to compare among themselves different explosive substances by the intensity of their thermal self-ignition. As a measure of intensity was used the height or energy of the bounce of the ball, lying on an aperture of the test-tube, in which flashed a small weighed amount of explosive substance.

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Experimental Part

The method of conducting experiments was as follows. A weighed amount of explosive substances was introduced into a glass test-tube, the bottom part of which to a depth of 5—7 cm was submerged in a thermostat with Wood's alloy, and the upper part was inserted in a massive metallic case with an aperture, covered by a steel or glass ball (Fig. 1). Height of bounce of ball at flash was determined visually with the help of a scale. Delay of flash was determined by a stop watch. Temperature of thermostat was maintained constant with an accuracy to one degree.

Height of bounce of ball was noted only in those experiments, in which the test-tube remained whole. If at flash the test-tube split, the height of the bounce varied greatly from experiment to experiment and can no longer be used as a measure of intensity of flash.

In the majority of experiments we used a test-tube with a diameter of 1.7 and a length of 15 cm, in a number of cases we used a test-tube with a diameter of 2 and a length of 20 cm. A weighed amount of explosive substance usually was introduced into a test-tube already heated to temperature of thermostat, however, all liquid, and also certain solid matter were placed in test-tube before its submersion into thermostat. Differences in the height of bounce of ball with such change of conditions of experiment were noticeable (when using large test-tubes the height of bounce of ball is decreased — see, for example, Fig. 12a and b — when introducing substance into cold test-tube it is increased), but not very significantly.

Intensity of flash was usually characterized by the product of height of bounce of ball by its weight: $E = mh$. During strong flashes ($E \gtrsim 10^2 - 10^3$ g·cm) this magnitude virtually does not depend on weight of ball, during weak flashes light balls give larger E than heavy.

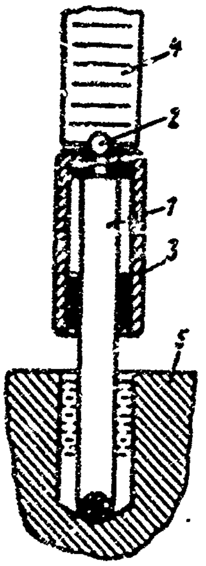

Fig. 1. Diagram of instrument for determining intensity of flash of explosive substance. 1—test-tube with explosive substance, 2—ball, 3—case with aperture in cover (diameter of aperture 10 mm) and packing, 4—scale, 5—thermostat with Wood's alloy.

During the experiments the following main pattern of phenomenon was detected.

At a temperature, lower than critical, the substance is calm, without appearance of flame, and the ball remains motionless. With the achievement of a certain critical temperature of self-ignition for given conditions flash occurs, usually accompanied by flame and sound and throwing the ball to a certain height. By the character of change of this height at a change of temperature and other conditions of the experiment, and also by the maximum height of bounce of ball with given weighed amounts, various explosive substances differ from each other quite substantially.

In Fig. 2—4 depict dependence of intensity and delay of flash on temperature of thermostat for small (0.01 — 0.05 g) amounts of several quick-burning explosive substances. Characteristic for the majority of them is that at all temperatures up to very high the intensity of the flash, after a more or less short section of initial growth, remains practically constant.

There is a somewhat more complicated picture in the case of tetrazene (Fig. 4). Height of bounce of ball during a flash of 0.01 g of this explosive at 136—200° is small and changes little with temperature, however at 152 and 155° very sharp flashes were observed, accompanied by splitting of test-tube. By increasing the weighed amount to 0.02 g the range of such detonation-like self-ignition was expanded.

A curious phenomenon was objected in the case of styphnate of lead and potassium. At 275—290° these substances along with usual flashes, appearing after prolonged (tens and hundred of seconds) heating, in a number of experiments with that same temperature, gave a flash with a delay one-two orders less (from a fraction of a second to seconds). A similar phenomenon was observed also in the case of styphnic acid.

The main distinction between secondary and throwing explosives and initiating explosives, as far as the character of dependence of intensity of flash on temperature is concerned, consists in the fact that, starting from a certain value of the latter, the intensity of self-ignition of these explosives falls, and the height of bounce of the ball is decreased, in most cases, practically to zero[1]. In the frame work of this general regularity various secondary explosives by the character of dependence of flash intensity on temperature can noticeably differ from each other.

Some of them (pyroxylin, tetryl, dyna, high-percentage solutions of nitrocellulose in nitroglycerine, trotyl[2]) are characterized by the fact that with an increase of temperature an increase of intensity of their flash to

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[1] Intensity of flash of certain powdery explosives with further increase of temperature can again somewhat increase.

[2] Trotyl (Fig. 3) is distinguished from other explosives by the fact that with the achievement of a certain sufficiently high temperature (under the conditions of our experiments ~365°) its self-ignition is suddenly stopped and the ball is no longer thrown. The so-called upper limit of self-ignition [1] will be reached.

maximum occurs gradually, in a significant (sometimes tens of degrees) range of temperatures (Fig. 5—8).

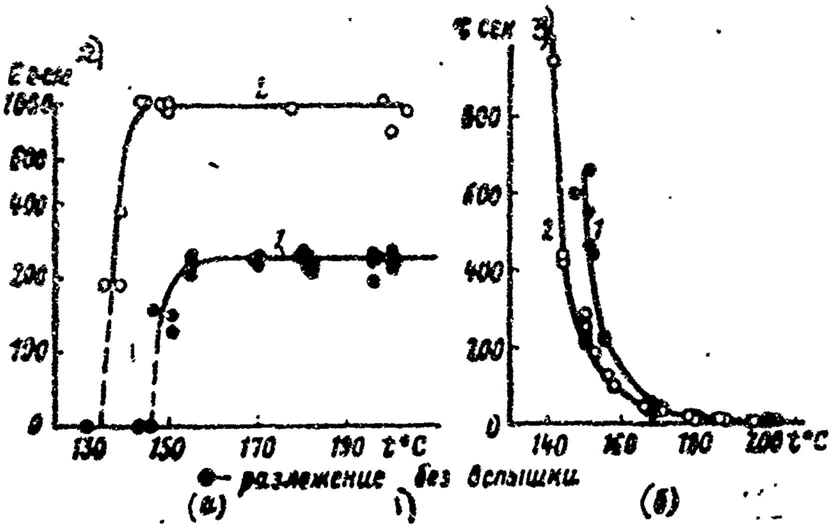

Fig. 2. Dependence of intensity (a) and delay (b) of flash of mercury fulminate on temperature. Amount of explosive: 1—0.02, 2—0.05 g. 1)●decomposition without flash; 2)E g·cm; 3)τ sec.

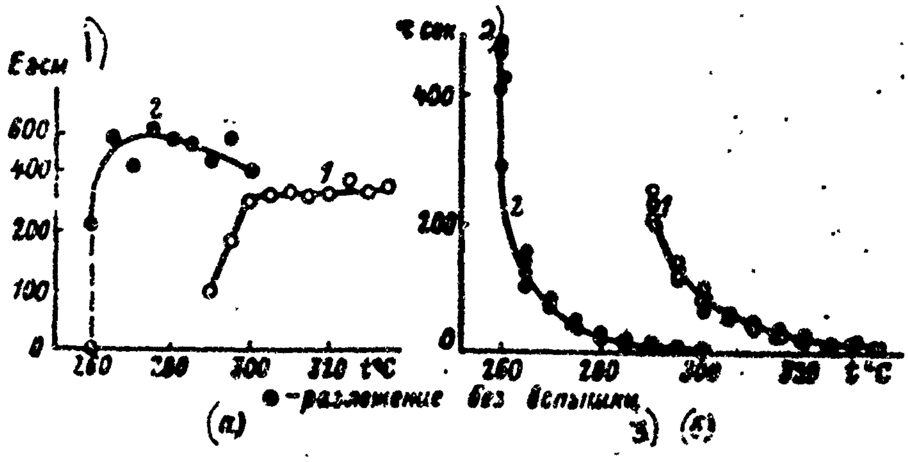

Fig. 3. Dependence of intensity (a) and delay (b) of flash of picrate of sodium (1) and lead (2) on temperature. Amount of explosive 0.02 g. In Fig. a each point is the average of 3—5 experiments. 1)Eg·cm; 2)τsec; 3)●decomposition without flash.

Other explosives (diglycoldinitrate, nitrogelatin, partly PETN) during transition through critical temperature of self-ignition give a flash of maximum intensity either immediately, or in a very narrow (one-two degrees) temperature range, after which the height of bounce of ball is gradually decreased (Fig. 9—11).

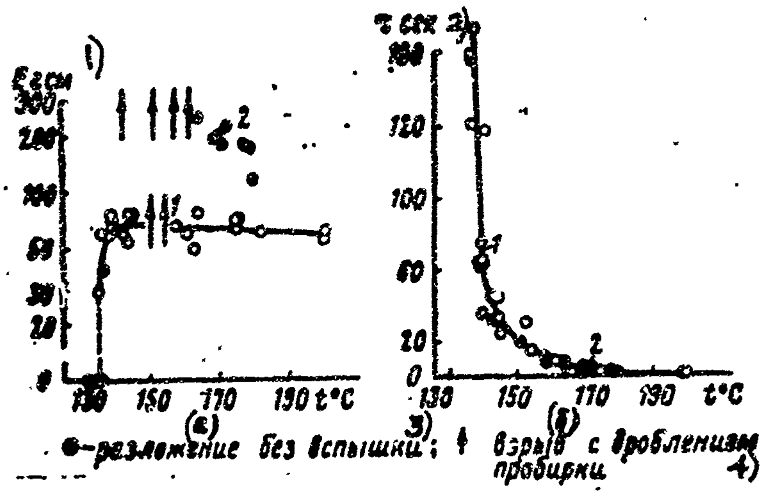

Fig. 4. Dependence of intensity (a) and delay (b) of flash of tetrazene on temperature. Amount of explosive: 1—0.01, 2—0.02 g. 1)Eg · cm; 2)τsec; 3)●decomposition without flash; 4)↑explosion with splitting of test-tube.

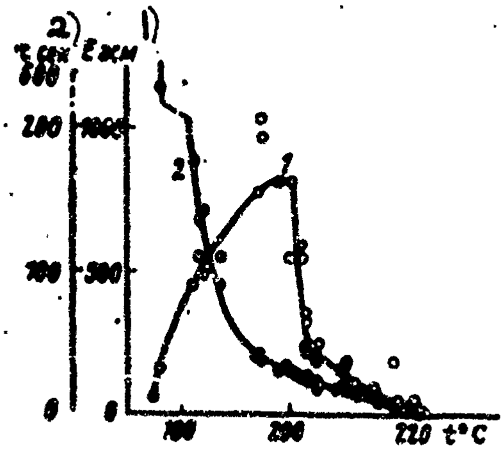

Fig. 5. Dependence of intensity (1) and delay (2) of flash of 0.05 g of pyroxylin on temperature. 1)Eg·cm; 2)τsec.

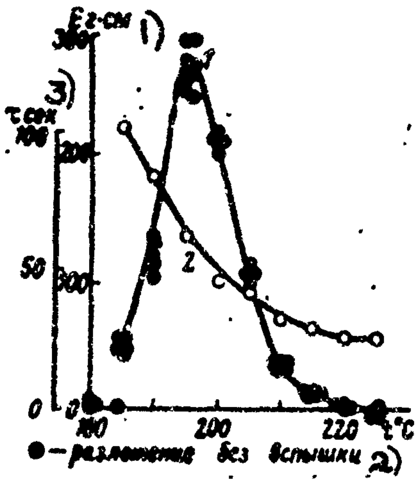

Fig. 6. Dependence of intensity (1) and delay (2) of flash of solution of collodion/nitroglycerine (50:50) on temperature. Amount of explosive 0.02 g. Each point on curve τ = f (t) is an average of 5 — 10 experiments. 1)Eg·cm; 2)●decomposition without flash; 3)τsec.

Nitroglycerine displays an unusual behavior (Fig. 12, experiments were conducted in test-tubes with diameters of 1.7 and 2 cm) upon reaching the critical temperature of self-ignition one drop (~0.02 g) of nitroglycerine immediately throws the ball to a significant height, greater than the maximum height during flash of PETN and diglycoldinitrate and nearly to the maximum height during flash of nitrogelatin. However at a further increase of temperature, in contrast to that, which is observed in the case of nitrogelatin, diglycoldinitrate or PETN, the intensity of the flash of NG does not fall, but grows rapidly attaining ~ 1000 g·cm, in some of these experiments the flash splits the test-tube in pieces. At a temperature of about 290° intensity of flash is abruptly decreased, and at 300–310° it becomes zero. Attention is drawn to the significant spread of results, especially with experiments in large test-tubes in the region of 230—280°.

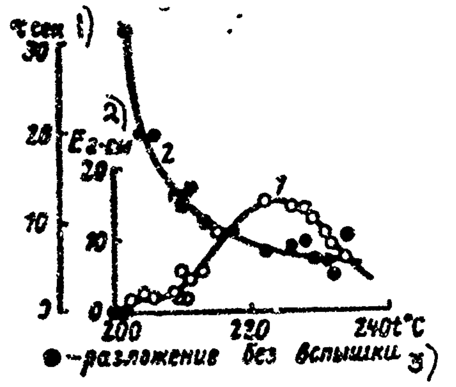

Fig. 7. Dependence of intensity (1) and delay (2) of flash of tetryl on temperature. Amount of explosive 0.1 g. 1) τ sec; 2) E g·cm; 3) ● decomposition without flash.

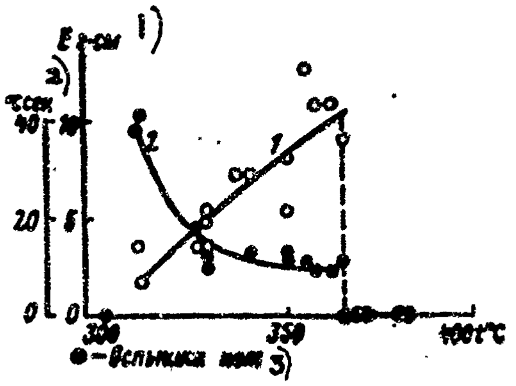

Fig. 8. Dependence of intensity (1) and delay (2) of flash of trotyl on temperature. Amount of explosive 0.1 g. 1) E g·cm; 2) τ sec; 3) ● no flash.

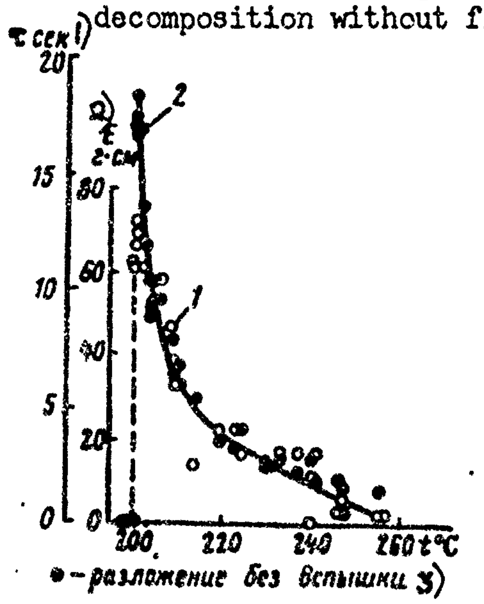

Fig. 9. Dependence of intensity (1) and delay (2) of flash of diglycoldinitrate on temperature. Amount of explosive 0.05 g. 1) τ sec; 2) E g·cm; 3) ● decomposition without flash.

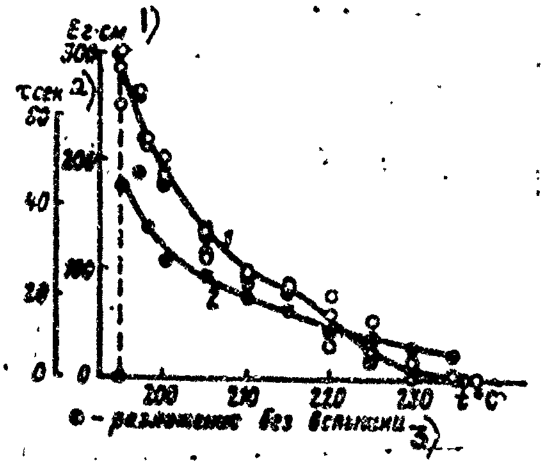

Fig. 10. Dependence of intensity (1) and delay (2) of flash of nitrogelatin (10% collodion) on temperature. Amount of explosive 0.02 g. Each point on curve $\tau = f(t)$ is an average of 3-5 experiments. 1) E g·cm; 2) τ sec; 3) ● decomposition without flash.

STOP

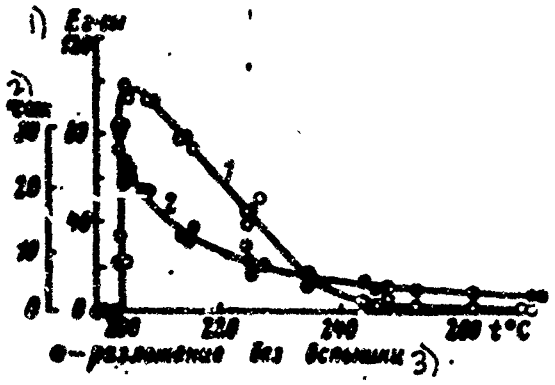

Fig. 11. Dependence of intensity (1) and delay (2) of flash of PETN on temperature. Amount of explosive 0.05 g is introduced into a heated test-tube with a diameter of 1.7 and a height of 15 cm (cf. Fig. 16). 1)E g·cm; 2)τ sec; 3)●decomposition without flash.

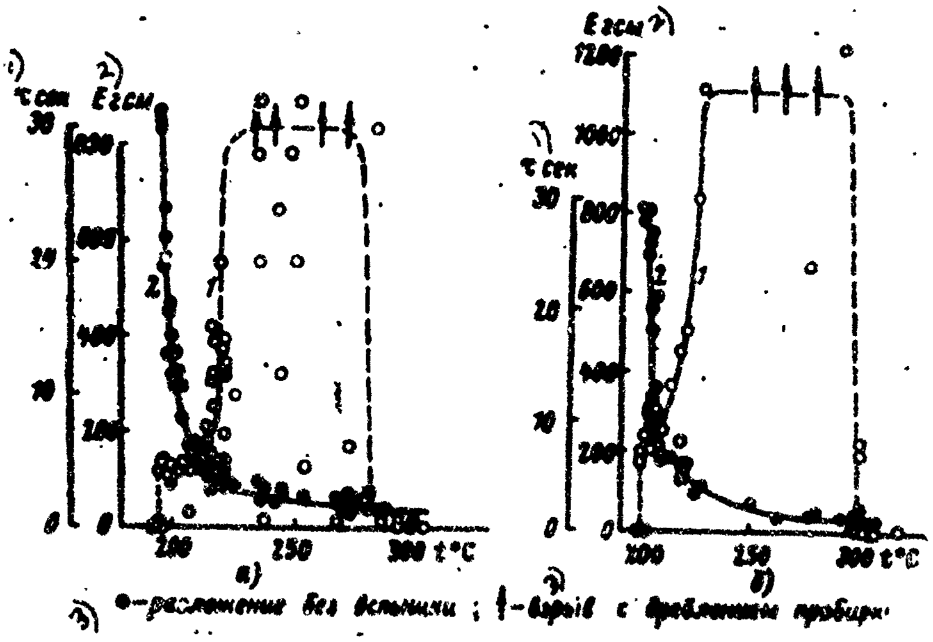

Fig. 12. Dependence of intensity (1) and delay (2) of flash of nitroglycerine on temperature. a—test-tube with a height of 20 and a diameter of 2 cm, b—test-tube with a height of 15 and a diameter of 1.7 cm. Amount of explosive ~ 0.02 g (one drop). 1)τ sec; 2)E g·cm; 3)●decomposition without flash; 4)╂explosion with splitting of test-tubes.

The very same is observed in the case of nitroglycol (Fig. 13) with the only difference being that splitting of test-tube does not occur, but the spread of results is so great that in the range 210—300° dependence of intensity of flash of nitroglycol on temperature in coordinates E—T is expressed not by a curve, but by a certain quite broad region.

STOP

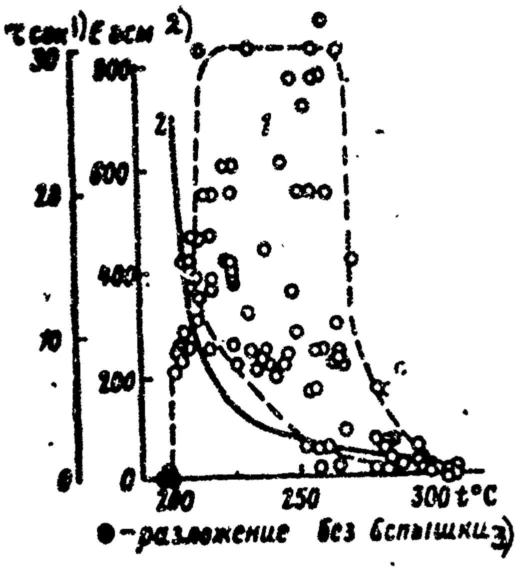

Fig. 13. Dependence of intensity (1) and delay (2) of flash of nitroglycol on temperature. Amount of explosive ~ 0.05 g (two drops). 1) τ sec; 2) E g·cm; 3) ● decomposition without flash.

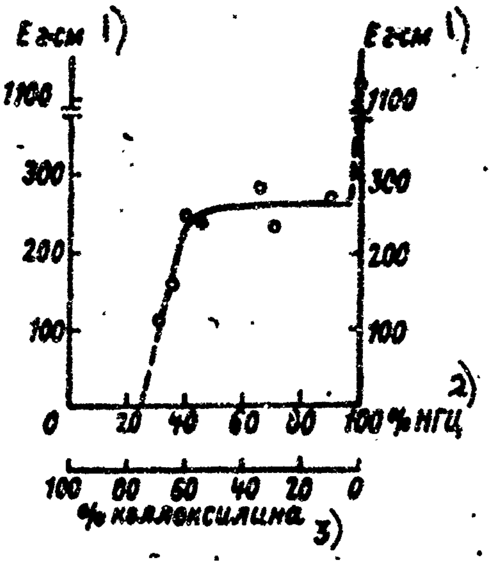

Fig. 14. Dependence of maximum intensity of flash of solutions of collodion in nitroglycerine on their composition. Amount of explosive. 1) E g·cm; 2) NG; 3) % collodion.

Maximum intensities of flash of investigated substances and certain other characteristics of experiments are presented in Table 1.

The greatest intensity of flash in the secondary explosives was possessed by nitro esters—nitroglycerine, methylnitrate, pyroxylin, nitroglycol; the least intensity—nitroamine and aromatic nitro compound, especially thermoresistant—hexyl, hexanitrodiphenylsulfide, hexogen, trotyl. From aromatic nitro compounds styphnic acid, is noteworthy in the amount of ~0.04 g throwing, although very irregularly, the ball almost as high as nitroglycol.

Quick-burning explosives by intensity of flash differ from each other less than secondary explosives and not one of them attains the maximum, observed for nitroglycerine.

It is interesting to trace how the maximum intensity of flash of solutions of collodion in nitroglycerine depends on their composition (Fig. 14)[1]. With 10% collodion the maximum intensity of flash decreases very strongly. By

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[1] These experiments are conducted by I. V. Babaytsev.

Table 1

Maximum intensities of flash of certain initiating and secondary explosives*

1 – Взрывчатое вещество	2 – Навеска, г	3 – Интервал температур, в котором изучалась и была получена вспышка**, °C	4 – Максимальная интенсивность вспышки (E_{max} г·см)×10^{-2}	5 – Температура, при которой наблюдается вспышка максимальной интенсивности, °C
6 – Гремучая ртуть	0,02 0,06	147—200 136—200	2,5 10	155—200 145—200
7 – Тетразен	0,01 0,02	136—200 142—180	0,8 2,4	140 165
8 – Пикрат натрия	0,02	290—335	3,1	306—335
9 – Пикрат калия	0,02	310—370	2,9	320
10 – Пикрат свинца	0,02	260—300	5,6	270
11 – Гексилат калия	0,02	325—375	8	345
12 – Нитроглицерин	~0,02	199,5—320	11	225—290
13 – Нитрогликоль*	~0,06	202,5—308	8	215—270
14 – Метилнитрат*	~0,02	267—270	8,1	
15 – Дигликольдинитрат*	~0,05	200,5—242	0,7	200,5
16 – Тэн	0,05 0,3	204—276 190—248	1 1,6	206 202
17 – Дина*	0,05 0,2	209—243 202—320	1 0,5	250 230
18 – Гремучий студень (10% коллоксилина)	0,02	195—235	2,8	196
19 – Пироксилин порошкообразный	0,05	176—225	8	195
20 – Пироксилиновый порох	0,1	170—205	0—0,2	
21 – Тетрил	0,1	202—265		225
22 – Тротил	0,1	300—365		365
23 – Гексоген	0,1	230—305		
24 – Октоген	0,1	265—330		
25 – Гексил	0,1	250—365		
26 – Гексанитродифенилсульфид	0,1	280—410		
27 – Пикриновая кислота***	0,1	300—325		
28 – Пикрат аммония****	0,02	260—325		
29 – Стифниновая кислота	~0,04	280—320	до 4	

1) Explosive; 2) Amount, g; 3) Range of temperatures, in which it was studied and flash was received**; 4) Maximum intensity of flash (E_{max} g·cm) X 10^{-2}; 5) Temperature, with which flash of maximum intensity is observed; 6) Mercury fulminate; 7) Tetrazene; 8) Picrate of sodium; 9) Picrate of potassium; 10) Picrate of lead; 11) Hexylate of potassium; 12) Nitroglycerine; 13) Nitroglycol*; 14) Methylnitrate*; 15) Diglycoldinitrate*; 16) PETN; 17) Dyna*; 18) Nitrogelatin (10% collodion); 19) Pulverized pyroxylin; 20) Pyroxylin powder; 21) Tetryl; 22) Trotyl; 23) Hexogen; 24) Octogen; 25) Hexyl; 26) Hexanitrodiphenylsulfide; 27) Picric acid***; 28) Picrate of ammonium****; 29) Styphnic acid.

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*Experiments with substances, marked by an asterisk, were conducted in test-tubes with a diameter of 2 and a height of 20 cm, the remaining substances were tested in test-tubes with a diameter of 1.7 and a height of 15 cm.

**Critical temperatures of self-ignition are set up by curve.

***Out of 26 experiments there were very weak flashes in three, in the remaining — thermal decomposition.

****Out of 15 experiments there were very weak flashes in five, in the remaining — thermal decomposition.

increasing contents of collodion to 60% this magnitude remains approximately constant, and then again abruptly falls, being decreased more than twice with 70% collodion, and with 75% practically to zero. This dependence can be compared with the fact that with an increase of amount it is very easy to cause explosion of solutions, containing 60% and less of collodion in nitroglycerine.

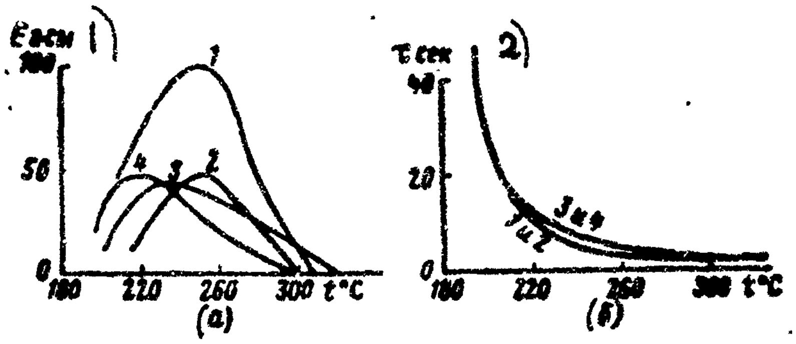

Fig. 15. Effect of magnitude of amount and nature of gas, filling test-tube, on intensity (a) and delay (b) of flash of dyna. Amount of explosive: 1 and 2 — 0.05 g, 3 and 4 — 0.2 g. Gas, filling test-tube: 1 and 3 — air, 2 and 4 — CO_2. 1)Eg·cm; 2)τsec.

Under certain conditions 60% gelatin explodes with splitting of test-tube even with an amount of 0.1 g. At the same time 70% solution does not split test-tube even with an amount of 1 g.

Generally speaking, with an increase in amount of explosive it is natural to expect an increase in intensity of self-ignition. Indeed, for many explosives (initiating and quick-burning, nitroglycerine, pyroxylin, nitrogelatin) with an increase in amount the intensity of flash considerably increases. In the case of PETN with amounts from 0.05 to 0.3 g it grows weakly, however, 1—2 of PETN are exploded, splitting test-tube into small pieces. Such an explosion is given by 2 g of diglycoldinitrate, but after a prolonged period of burning. Pulverized pyroxylin gives a strong explosion even with an amount of 0.5 g. An increase in amount significantly increases intensity of flash in the case of picric acid.

However certain secondary explosives display other behavior: with an increase in amount the intensity of their flash does not increase, but is decreased. A typical example of such a substance is dyna (Fig. 15), in the case of which an increase in amount 4 times (from 0.05 to 0.2 g) twice decreases the maximum intensity of flash.

Table 2

The effect of CO_2 on flash characteristics of certain explosives*

1 – Взрывчатое вещество	Навеска, г 2-	Температура, °C 3-	4- В воздухе		9- В CO_2	
			$(E_{max}$ г·см$)\times 10^{-2}$	10 τ, сек	$(E_{max}$ г·см$)\times 10^{-2}$	10 τ, сек
5 – Дигликольдинитрат	0,05	206—207	0,7	8,6	0	18,7
6 – Нитрогликоль	0,05	211—212	3,4	9,8	2,2	8,8
7 – Метилнитрат	0,02	267—270	8,1	2,9	0,9	3,2
8 – Пироксилин	0,05	189—191	2,9	66	1,5	96

* Значения E и τ — средние из нескольких опытов.

1) Explosive; 2) Amount, g; 3) Temperature; 4) in air; 5) Diglycoldinitrate; 6) Nitroglycol; 7) Methylinitrate; 8) Pyroxylin; 9) In CO_2; 10) τ sec.

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*Values of E and τ — average from several experiments.

In order to explain the effect of processes occurring in gas phase on intensity of flash, experiments were conducted with which air in test-tubes was replaced by carbon dioxide (Table 2, Fig. 15, 16 and 17). Results of these experiments show that composition of gas phase plays an essential role in self-ignition not only of high-volatile methylnitrate, which otherwise as in gas phase is not able to flash, but also with the flash of such low-volatile substances, as diglycoldinitrate and PETN, and even quite nonvolatile pyroxylin.

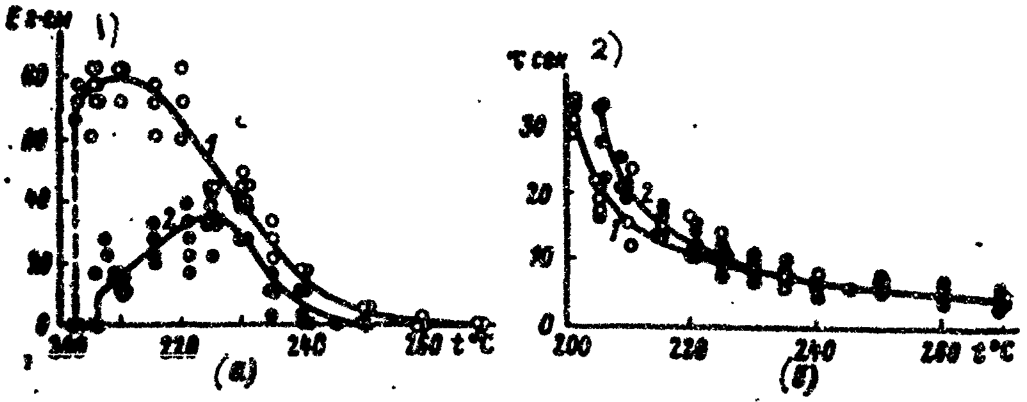

Fig. 16. Effect of nature of gas, filling test-tube, on intensity (a) and delay (b) of flash of PETN. Amount of explosive 0.05 g. 1 — in air, 2 — in CO_2. Points on axis of abscissas at low temperature — decomposition without flash. Amount is introduced into test-tube with a diameter of 2 and a height of 20 cm before submersion of the latter in thermostat (cf. Fig. 11). 1) E g·cm; 2) τ sec.

Interesting behavior is displayed by dyna (Fig. 15). With a small (0.05 g) amount the maximum intensity of its flash in carbon dioxide is significantly less than in air, with a large (0.2 g) amount both intensities practically coincide with each other, and also with intensity of flash of 0.05 g in an atmosphere of CO_2.

In the case of nitroglycerine replacement of air by carbon dioxide considerably decreases the intensity of flash at low temperatures and has practically no effect on it at high temperatures (Fig. 17).

One should note that replacement of air by CO_2 in most cases depresses not only the intensity of flash, but also the ability of substances to self-ignite, noticeably raising critical temperature of flash.

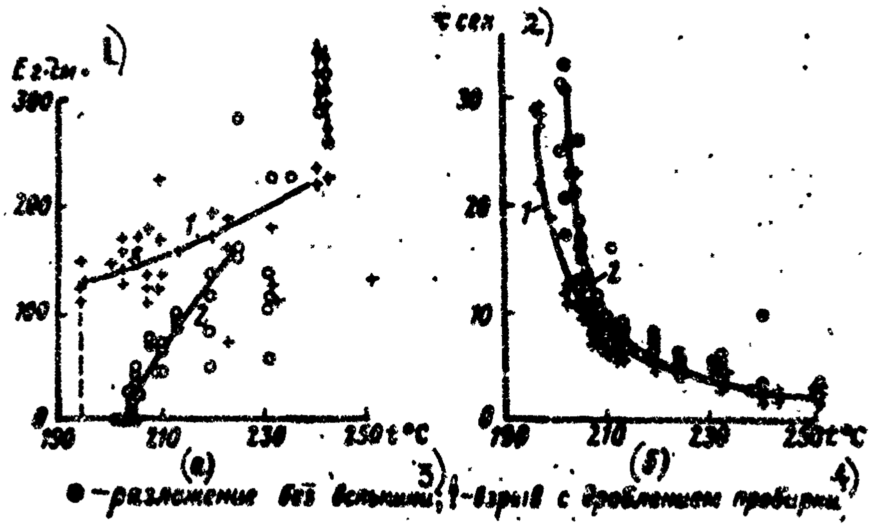

Fig. 17. Effect of composition of gas phase on intensity (a) and delay (b) of flash of nitroglycerine. Amount of explosive ~0.02 g. 1 — in air, 2 — in CO_2. 1) E g·cm; 2) τ sec; 3) ● decomposition without flash; 4) ♦ explosion with splitting of test-tube.

A characteristic peculiarity of a majority of liquid and melted explosives noted by A. F. Belyaev [3], is the formation before flash sometimes of very significant quantities of foam. As visual observation shows, the quantity and consistence of foam change from substance to substance and depend considerably on the conditions of the experiment. In particular, at an increase of temperature the quantity of foam is significantly decreased, and at sufficiently high temperature it will not be formed at all. It is essential to note that the formation of foam promotes an increase in intensity of flash, and in the case of large (1—2g) amounts of such explosives as diglycoldinitrate and PETN, makes their explosion possible.

Discussion of Results

The flash of explosives, as is known, represents burning of the heated substance, occurring by means of self-ignition. Intensity of flash is determined by speed of gas formation during burning, and the latter for a majority o. explosives is determined, basically by the speed and the burning surface[1].

The value of the normal burning rate at flash of a substance is completely obvious. It is clearly manifested, for example, during the comparison of a majority of secondary explosives with quick-burning ones, especially picric acid and hexyl with picrate and hexylate metals (see Table 1).

It is not less obvious, however, that the normal burning rate is not the only determining factor. Hexogen and tetryl burn faster than diglycoldinitrate and nitroglycol, meanwhile a flash of 0.1 g of hexogen does not even raise the ball, tetryl gives E equal to only 15 gcm, whereas diglycoldinitrate (with an amount of 0.05 g) gives E = 70 gcm, and nitroglycol in intensity of flash approaches mercury fulminate. The most probable cause of such a distinction is the difference in magnitude of burning surface at flash of these substances.

The larger the surface of burning at self-ignition of explosive the greater the possibility of penetration of flame into the depth of the charge, i.e. on one hand, the bigger the temperature of gases and inflammability of substance, but on the other — the more friable and porous the substance, the less its

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[1] Speed of gas formation, naturally, depends also on specific volume of gaseous products at temperature of burning. This side of the question will not be considered here.

durability, density, viscosity, etc. Graphically illustrated is this affirmation of the experiment with pulverized pyroxylin and pyroxylin powder (see Table 1). The first of them at flash throws the ball almost as high as mercury fulminate, but the second does not throw it at all. Obviously, friability and porosity of pulverized pyroxylin at sufficiently high inflammability of the heated substance ensure the penetration of the flame into the depth of the amount and its violently intense combustion.

Liquid explosives behave similarly (a typical example of them is nitroglycerine), the burning rate of which at increased temperature exceeds the critical speed of burning of liquid according to Landau — Andreyev [2]. In this case burning of liquid proceeds in the turbulent regime, gaseous products penetrate into the mass of the explosive and the flash takes on the character of explosion.

However the burning rate of many secondary explosives (nitroglycol, diglycoldinitrate, PETN, etc.) even at the temperature of self-ignition is still far from critical, meanwhile they flash quite intensely, in certain conditions — with explosion. Obviously, during heating these substances endure transformations which allow the flame to penetrate to the depth of the charge even at comparatively small normal speed of its propagation. We can consider the main transformation to be the foaming of the explosive. Apparently, light, low-viscosity foam is precisely that state of the substance, with which burning penetrates especially easily into its depth, and, encompassing a large surface, creates an increase of pressure, characteristic of explosion.

Propagation of burning in a layer of foam, besides all other, depends on its consistence. Light mobile foam, formed when heating such explosives as diglycoldinitrate and PETN, burns quickly and, if its quantity is sufficiently great, it explodes. Substances, melted at high temperature, especially thermoresistant explosives usually produce a foam which is thicker, viscous, and burns comparatively slowly and calmly.

Another important factor, determining the intensity of self-ignition of explosives under the conditions of our experiments, is, as experiments show on flash in an atmosphere of carbon dioxide, transformation of substance into reactive gases and vapor and the formation of a mixture of them with air. The inclination of gas systems to turbulization of front and an increase of burning surface is well-known. It is natural to expect, therefore, that transformation of condensed substance into gas capable of burning by itself significantly increases the speed of its combustion. On the other hand, burning of a gas mixture as a result of increase in pressure, scattering of substance by streams of burning gases, their penetration into the depth of friable explosives, etc., can lead to an increase in burning rate or even explosion of the most condensed substance. Finally, with an explosion of gas mixture there can appear also a shock wave, sufficiently intense to excite an explosion or detonation in the condensed substance, all the more so in heated and foamed substances.

It may be concluded, consequently that in the case of a majority of secondary and throwing explosives for a flash of significant intensity it is necessary, during heating of the substance, to form large quantities of either low-viscosity and light foam, or a combustible gaseous mixture[1].

Let us consider now in the light of the above assumptions the main regularities obtained in this work — dependence of flash intensity of an explosive on temperature. For a majority of explosives the transition through critical temperature of self-ignition is accompanied by a more or less smooth increase in the intensity of the flash. The main cause of this, probably, is

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[1] Formation of a layer of foam or gaseous mixture undoubtedly has an effect on not only intensity but on other characteristics of thermal self-ignition—critical conditions and delay of flash.

that with an increase of temperature the degree of decomposition of substance before flash is decreased, i.e. the quantity of burning explosive is increased and its dilution by products of disintegration is decreased.

In the case of self-ignition of those substances, in which, with a small amount, a flash of significant or even maximum intensity appears immediately after achieving the critical temperature of self-ignition, a chief role in the process of burning in these conditions is played, apparently, by gaseous products in mixture with air. It is easy to see that the biggest quantity of the latter before flash will be formed precisely near critical conditions. Flash in small quantities of diglycoldinitrate, nitroglycol, nitroglycerine, nitro gelatin, and possibly also PETN at temperatures, near critical, apparently, occurs precisely in this manner.

The intensity of the flash in secondary and throwing explosives, starting with a certain temperature, is lowered. It is possible to explain this phenomenon, assuming that at high temperatures a substance flashes earlier, than its main mass has time to be prepared for flash — to be turned into foam or gases and vapor, and at sufficiently high temperature even simply to be heated. The burning rate of a substance in this case is decreased, and the intensity of the flash falls.

Initiating explosives, fast burning at any temperature, do not need such preparation and give a flash of significant and constant intensity at all temperatures higher than a certain limit (below which before flash too large a portion of the substance is decomposed). However, the dependence of intensity of flash on temperature, obtained for tetrazene, allows us to consider that also in the case of certain initiating explosives the preparation of the substance in the induction period can considerably affect the intensity of self-ignition.

The author thanks professor K. K. Andreyev for his help during this work and the discussion of results.

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Tape No. MT-63-254 Chapter 3 Article 36

Pages 528-533

K. K. Andreyev and V. V. Gorbunov

36. On the Thermostability of Crystals of Explosives

In a number of investigations on burning and thermal decomposition of single crystals of explosives, cracking and destruction of them during these processes is noted [3]. K. K. Andreyev expressed the assumption that one of the causes of cracking can be thermal shock, i.e. fast heating of crystals from the surface [1]. With distinctions in inclination to cracking he connected the different behavior of powdery explosives upon igniting them in a closed vessel. It was assumed that cracking of crystals occurs while heating them with hot gaseous products of burning, penetrating the pores between particles, constituting a charge of powdery explosive. An increase of surface during cracking of crystals can lead to an increase of gas formation and transition of burning to explosion.

In connection with these considerations we set up experiments on the determination of thermostability of explosive crystals and its role in the process of burning. Thermostability or sensitivity of crystals to thermal shock in preliminary experiments was determined by throwing large crystals into heated water. Maximum fall of temperatures (difference between initial temperature of crystal — usually 18—20 — and temperature of water), with which in the crystal any visible changes (cracks, splitting) were absent was established.

It turned out that crystals of many explosives are very sensitive to thermal shock. The biggest fall of temperatures is sustained by crystals of trotyl and picric acid (nearly 45°), crystals of TEN and hexogene were cracked already at a fall of 15—20°.

To the deficiencies of this methodology one should refer the uncertainty of time of thermal action on crystals and essential distinctions under the conditions of the experiments from those, that take place in experiments on the study of transition of burning of an explosive to an explosion. Therefore further experiments we conducted by another method, which allowed to estimate thermostability of explosive crystals by the character of changes, appearing in them during free fall through a furnace. This furnace resembled a quartz tube (diameter 25 mm, length 300 mm), heated by a platinum spiral. A diagram of the installation for determination of thermostability of explosive crystals is given in Fig. 1. For measurement and adjustment of temperature of furnace a thermocouple 2 and electronic potentiometer EPV-01 7.

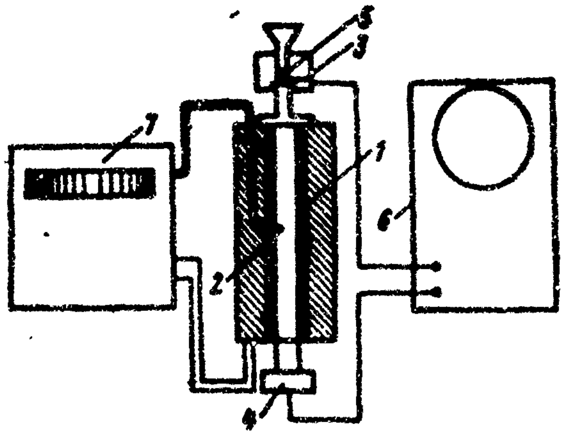

Fig. 1. Diagram of installation for determination of thermostability of explosive crystals.
1 — quartz tube with platinum spiral, 2 — thermocouple, 3 — stopper, 4 — telephone element, 5 — explosive crystal, 6 — ENO-1, 7 — EPV-01.

The gradient of temperatures on the length of the furnace did not exceed 1°/cm at a furnace temperature of 500°. The crystal 5 was placed on the petals of the stopper 3, fixed on the upper section of the furnace, and upon opening the stopper fell through the furnace. As the receiving mechanism, telephone element 4 was used on the diaphragm of which fell the crystal or its fragments. The time from the moment of opening of the stopper to the fall of the crystal or its fragments on the diaphragm was registered by oscillograph ENO-1 6. For crystals weighing from 2 to 200 milligrams, this time, after subtracting the time of flight through cold parts of the instrument, constituted 0.24 — 0.28 sec. By analogy with the preceding experiments in the beginning thermostability was estimated by minimum temperature of the furnace, with which on the crystal appeared cracks. For the majority of studied explosives, the appearance of cracks was observed at furnace temperatures of 200 — 300°. However, in spite of the near values of temperature of appearance of cracks, at a further increase of furnace temperature for some substances was observed intense splitting of crystals, for others (tetryl, dyne, ammonium perchlorate) only an increase of the number of cracks[1]. Therefore in subsequent experiments as measure of sensitivity to the action of thermal shock served a number of fragments, formed at a given temperature of the furnace[2], and a change of this number upon reinforcing its heating.

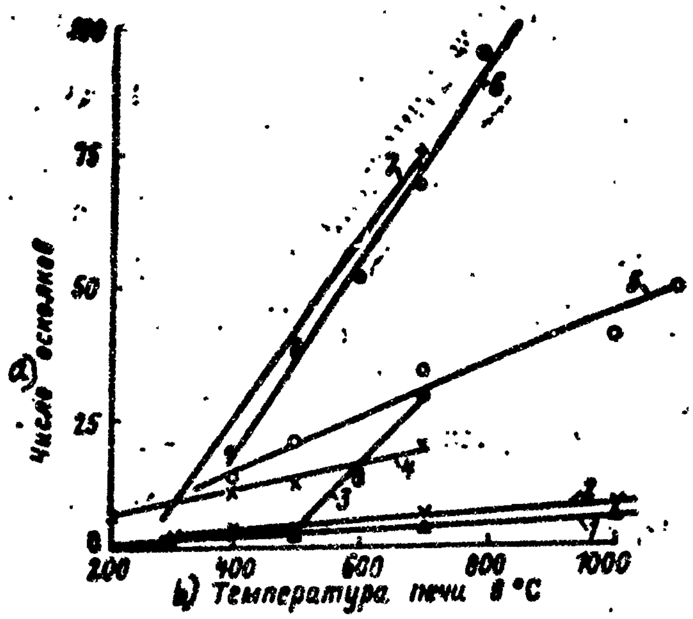

Fig. 2. Dependence of intensity of splitting of explosive crystals on furnace temperature.
1 -- trotyl, 2 -- picric acid, 3 -- styphnic acid, 4 -- potassium styphnate, 5 -- TEN, 6 -- hexogene, 7 -- potassium picrate.
a) number of fragments; b) Temperature of furnace in °C.

The dependence of intensity of splitting of crystals of certain explosives on furnace temperature is presented in Fig. 2. Every point on the graph of this figure averages the results of no less than 5 experiments. It is clear that for all explosives studied, the quantity of fragments linearly increases with the increase of furnace temperature. The most inclined to cracking, especially at high temperatures, are potassium picrate and hexogene. Moderate splitting was

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[1] In these and subsequent experiments crystals weighing from 20 to 60 milligrams were used. Change in the weight of the crystals in such limits did not change the qualitative picture of cracking.

[2] Upon falling through a cold stove no change in the crystals was observed.

observed for crystals of styphnic acid and potassium styphnate. The straight lines in the coordinates (number of fragments — temperature) of the furnace in Fig. 2 have different slopes, therefore the position of a substance in a series of thermostability with a change of temperature can change. Thus, at a furnace temperature of 500°, TEN crystals will form 5 times more fragments, than styphnic acid; at a temperature of 700° the number of fragments of both explosives is almost equal. It is possible that a sharp increase of the number of fragments of crystals of styphnic acid at temperatures above 500° is connected with the achievement of conditions, with which occur qualitive changes in their structure, as a result of which, the sensitivity of crystals of this explosive to thermal shock is sharply increased. Crystals of trotyl, picric acid, tetryl, dyne and ammonium perchlorate are distinguished by high thermostability. Even at furnace temperatures of 1000 — 1100°, the crystals of these substances were crushed not more than into 5 — 7 fragments. On dyne crystals there appeared cracks at 300 — 600°, at higher temperatures occurred melting of crystals of this substance.

It was interesting to estimate thermostability of explosive crystals at high temperatures, near to those, which lead to ignition of a crystal during its fall through the furnace. A flash was observed for hexogene, octogene, potassium picrate, styphnic acid and lead styphnate. Due to the large number of fragments and melting drops near the flash, an estimate of thermostability by the number of fragments in this case is less reliable; however, at least, for crystals of hexogene (Fig. 2) the number of fragments upon an increase of furnace temperature up to the flash (900°) continued to increase approximately the same as at lower temperatures. Small (4 — 5 milligrams) crystals of lead azide were not cracked at a furnace temperature of 550° and were exploded at 600°. Up to the flash at 700° crystals of lead styphnate were not cracked also. One should indicate that the hexogene crystals near to it in weight in these conditions were crushed into 15 — 20 fragments.

In the preceding experiments thermostability of large explosive crystals was studied. In actual conditions we deal with small crystals and their fragments. It was interesting to study the influence of the dimensions of the crystals on the intensity of their splitting under the action of thermal shock. At a furnace temperature of 500 and 700° was studied the thermostability of crystals of TEN and hexogene of different dimensions. According to the adopted methodology, as a measure of sensitivity to thermal shock served a number of fragments, formed during splitting of a crystal. In the beginning was calculated the specific surface of a crystal (cm^2/g), assuming that it has the form of a sphere and the corresponding weight. The same way was determined by calculation the specific surface of fragments after the experiment. The dependence of intensity of splitting on the dimensions of crystals (calculated diameter of a sphere) of TEN and hexogene at a furnace temperature of 500 and 700° is depicted in Fig. 3 (graph a). Here is shown the increase of specific surface as a result of splitting the crystals at a furnace temperature of 500° (graph b). At all studied dimensions of crystals, hexogene yielded more fragments, than TEN. However this distinction is decreased with the increase of dimensions of the crystals. Thus, upon splitting of crystals, having a diameter of approximately 1 mm, hexogene yields 5.5 times more fragments, than TEN with an increase of diameter to 4 mm this ratio is decreased up to 2.5 times. The absolute increase of surface for small crystals is greater than for big ones. At the same time, a relative increase of specific surface increases with an increase of the dimensions of the original crystals.

The data obtained during the study of thermostability of crystals of different explosives, show that the latter are greatly distinguished in this respect.

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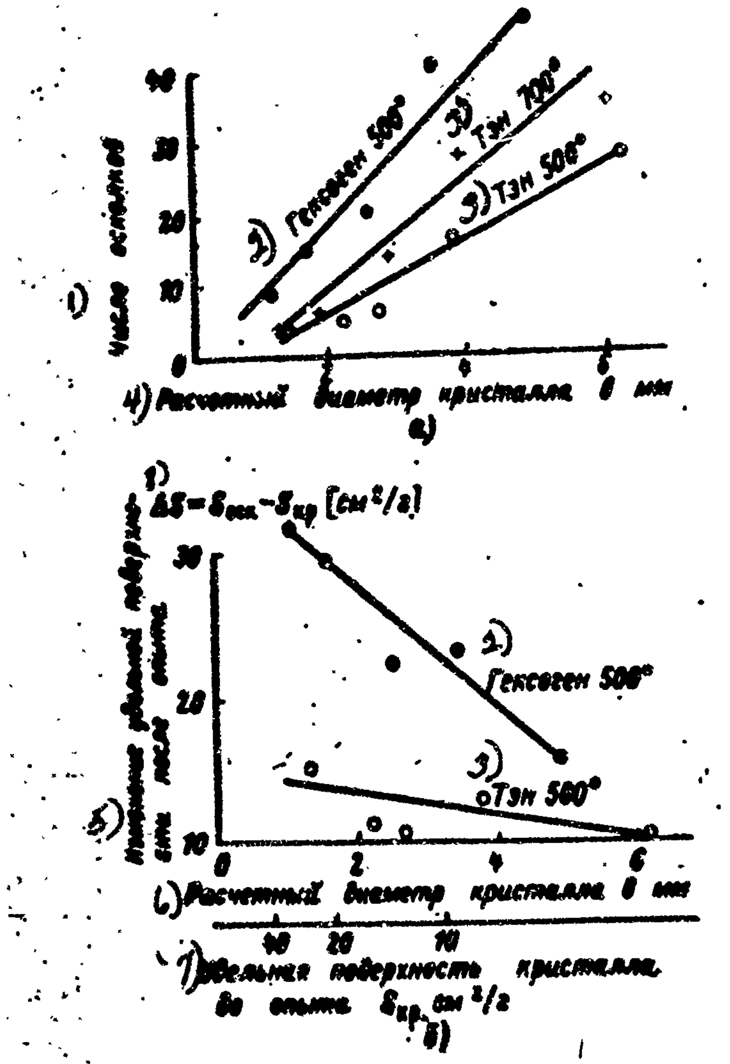

Fig. 3. Influence of dimensions of explosive crystals on intensity of their splitting under the action of thermal shock.
1) Number of fragments; 2) Hexogene; 3) TEN; 4) Calculated diameter of crystal in mm; 5) Change of specific surface after experiment; 6) Calculated diameter of crystal in mm; 7) Specific surface of crystal before experiment Scr cm^2/g; 8) Δ S=Sfrag-Scr [cm^2/g].

It is interesting to compare the sensitivity of a substance to thermal shock with the stability of burning it under increasing pressure. For that we studied burning of an explosive in a steel glass, covered with a lead disk, cut after achievement of a determined pressure [2]. The critical thickness of the disk was determined, with which occurred splitting of the tube, near the explosive. If the thickness of the disk is less than critical, then only its extraction is observed, besides sometimes burning of the remaining charge is stopped. In one of the experiments after extracting the disk, a large part of the charge (nearly 70%), consisting of hexogene crystals of 5 — 7 mm, remained in the tube. To the greatest splitting were subjected crystals of the upper layers of the charge, directly touching the products of burning of the igniter[1]. Crystals, lying in the depth of the charge, remained without change. Below are the results of a screen analysis of that part of a charge of hexogene, that remained in the tube after ceasing of burning.

1) Размеры кристаллов в мм	2) Вес фракции в г	3) Содержание в % вес.
	5) До опыта	
4) от 5 до 7	50	
	6) После опыта	
4) от 5 до 7	15,7	45,2
7) от 3 до 5	9,0	25,9
8) от 2 до 3	3,0	8,6
9) от 1 до 2	1,2	3,5
10) от 0,5 до 1	2,9	8,3
11) менее 0,5	3,0	8,5
	34,8	100,0

1) Dimensions of crystals in mm; 2) Weight of fraction in g; 3) Contents in % by weight; 4) from 5 to 7; 5) Before experiment; 6) After experiment; 7) from 3 to 5; 8) from 2 to 3; 9) from 1 to 2; 10) from 0.5 to 1; 11) less than 0.5.

Burning of TEN and hexogene (dimensions of crystals approximately 0.25 mm) changes into an explosion at a thickness of the lead disk of 1.1 mm. It is possible to assume [1], what the application to the surface of a crystal of a film of inert substance will decrease the sharpness of heating, cracking and consequently, the inclination to transfer burning into explosion. Indeed, our experiments showed that burning of TEN, containing 4.3% flegmatizer[2], distributed on the surface of the crystals, changes into an explosion only at a thickness of the lead disk of less than 5 mm, and hexogene with the same quantity of flegmatizer, does not yield an explosion, even if the tube is covered by a steel disk 6 mm thick. The inclination to transfer burning to an explosion is greatly lowered only in a case, if a flegmatizer in the form of a film covers the surface

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[1] In a given case, splitting of crystals occurred not under the influence of a jump in pressure (nearly 10 technical atmospheres), since the experiments showed that in hexogene crystals any changes at thorough sharp pressure of them to a pressure of 70 technical atmospheres and subsequent sharp fall of pressure are not observed.

[2] As a flegmatizer, a mixture of stearin and cerezin was used.

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of the crystals. Simple addition to hexogene of an inert substance, for example, starch in a quantity of 9%[1], leads to an increase of the critical thickness of the disk only up to 1.5 mm (instead of 1.1 mm for hexogene without additions). All these data confirm the fact that an increase of the surface of crystals as a result of cracking plays an essential role during transition of burning of a powdery explosive under increasing pressure to an explosion.

Conclusions

1. A method of estimating sensitivity of explosive crystals to thermal shock accomplished by heated gas was developed.

2. The sensitivity to thermal shock of crystals of a number of explosives at furnace temperatures of 300 — 1100° was determined. The most inclined to cracking are crystals of hexogene and potassium picrate. Crystals of trotyl, picric acid and tetryl are not very sensitive to thermal shock.

3. The influence of dimensions of crystals of TEN and hexogene on their sensitivity to thermal shock at a furnace temperature of 500 and 700° was studied. With an increase of the dimensions of the original crystals this sensitivity increases.

4. The obtained data were compared to certain regularities, observed upon transition of a burning explosive in a closed vessel to an explosion.

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[1] A mixture of hexogene with 9% starch has the same speed and calculated temperature of burning as does hexogene with 4.3% flegmatizer.

MT-63-254

Chapter 3 Article 37

Pages 534-539

K. K. Andreyev

37. Concerning the Question of Transition of Burning of Explosives to Explosion.

An essential peculiarity of an explosive is the fact that in their chemical transformation heat will emanate and gases will be formed. At the same time this transformation can be accelerated by heat (if its separation leads to an increase of temperature) and gases (if their formation leads to increase of pressure, and the transformation proceeds in the form of burning). However along with these factors, accelerating the process, are factors, counteracting acceleration. This in the first case is the heat supply in the outside, decreasing the increase of temperature and in the second case—the gas supply, leading to lowering of pressure.

If the influence of those and other factors is balanced, then the speed of the process increases only to a certain equilibrium value. If the factors of acceleration predominate, then the speed of chemical transformation does not remain on this limit, but continues to grow, striving for its own maximum.

At homogeneous flow of chemical transformation in the entire volume of explosive charge this occurs, if the speed of heat liberation becomes greater and grows with temperature faster than the speed its supply to the environment. Then the temperature of the explosive grows, correspondingly is increased the speed of transformation, and it can be completed by explosion.

Let us imagine a burning charge of powdery explosive with a certain specific internal surface, and burning occurs on all this surface. If the speed of formation of gases is greater than the speed of their feed beyond the charge, then such burning becomes self-accelerated. Pressure in the charge grows and correspondingly the burning rate is increased.

At thermal self-acceleration one of the main parameters is the size of the charge. Heat arrival is proportional to the cube of the size, heat discharge (during convection heat exchange) — its square. Therefore, in increasing the size, of the charge, we can always to arrive at its critical value, above which the process will become self-accelerated. In exactly the same way and at burning in considered conditions, when the quantity of generated gases is proportional to the volume of the charge (at a given specific internal surface of the explosive), and their quantity is diverted — its surface, should be a certain critical size, upon exceeding which the speed of gas generation becomes greater than the speed of gas discharge.

Another main parameter at homogeneous passage of chemical transformation and its thermal self-acceleration is the initial temperature, which determines the original speed of the reaction, and consequently, the speed of heat liberation. At thermal appearance of an explosion the critical values of both shown parameters (size of charge and initial temperature), as it is known, are mutually connected.

When the reaction occurs in the form of burning, such a second parameter, on which also depends the critical size, is the initial pressure. This pressure determines the burning rate, and consequently, the initial speed of gas formation. The specific surface of the substance, plays the same part as pressure, since the speed of gas formation is equal to the product of the burning rate on its actual surface.

The Main Conditions, Necessary For the Appearance of Self-Accelerated Burning of Powdery Explosives

There is, however, an essential distinction between both mechanisms of development of the self-accelerated transformation with respect to their excitation.

In order that thermal self-acceleration of the process occurs, a sufficient explosive charge of a certain size is heated to a certain temperature.

In order that the explosion occurs by means of burning, a sufficiently large charge is necessary, consisting of a set of particles, heated throughout its internal surface. This is not so simple to ensure. If specific surface is great, i. e. the dimensions of the particles and gaps between them are small, the problem is complicated still more. When we light a charge from without, then burning, especially with small gas-penetrability, is either limited by the macrosurface of the charge, or penetrates into it only at a small depth. In local igniting from within of a powdery charge a large part of the explosive, surrounding the focus of igniting, is scattered by unigniting from the increase of pressure, caused by burning, starting in the focus.

Burning can penetrate into the depth of a powdery charge in two cases.

1. Burning of an explosive occurs with great speed, due to which on the surface of the charge will be formed a significant dynamic increase of pressure. Along with this the chemical reactions proceed quickly and already at low pressures will be formed products of complete transformations, having high temperature, i. e. a great igniting ability. The third condition, in a known measure combined with the first two, is the high inflammability of the explosive.

If these conditions are fulfilled in a sufficient measure, then even at constant and low pressures burning penetrates into the depth of the porous charge and can change into explosion. Precisely thus is the matter in the case of initiating explosives.

Secondary explosives do not satisfy the conditions guaranteeing the transition of burning at low constant pressures to explosion. First of all, conversion of these explosives during burning occurs comparatively slowly and at atmospheric pressure is not completed, due to which the temperature of the products of their burning is much lower[1] than at full conversion attained at high pressures. Secondly, the burning rate of secondary explosives, and consequently, the dynamic increase of pressure on the burning front is significantly less than in initiating explosives. Thirdly, their inflammability is less.

In burning under increased constant pressures, created by placing an inert gas into the cylinder before igniting the explosive, the reactions proceed faster and more complete, the burning rate is also greater, but penetration of gases into the depth of the charge and ignition by them of particles of the explosive prevents cooling by the inert gas which is diluting the explosive.

2. The most real method, ensuring burning of a powder charge on the entire internal surface, consists of igniting the explosive in a closed vessel, in which burning takes place under increasing pressure, forcing the gaseous products to penetrate into the depth of the powder.

The greater the resistance of the walls of the vessel, determining maximum pressure, which can be attained in it, the thicker the layer of substance, into which burning can penetrate. If this layer is thicker than critical, then further growth of pressure in it no longer depends on the presence of a cover (let us imagine that it disappeared in that moment, when burning enveloped the surface of the charge), but occurs immanently, being determined by those parameters, that were mentioned above. Thus, the role of resistance of a cover in igniting in a closed vessel consists not so much in the fact that this resistance affects (through pressure) the fullness of transformation, the distance from the surface of the charge, on which this fullness will be attained, and on the burning rate, as much in that it determines the depth of penetration of gases, and together with them, burning and thickness of the charge.

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[1] Temperatures of burning at atmospheric pressure by calculation, based on the final composition of gaseous products of burning and for certain explosives approximated (due to the lack of heat of formation of condensed products), comprise for trotyl approximately 2000°, tetryl - 2400°, hexogene - 3200°, mercury fulminate - 3900°, diazodinitrophenal - 3300° and potassium picrate - 2800° K.

It is known that burning of certain explosives, for example, TEN and hexogene, upon igniting them in a closed vessel changes into an explosion much easier with a lower durability of the cover, than many other explosives, for example, tetryl or trotyl. At the same time the difference in speeds of their burning especially at moderately increased pressures) is not so great in order to explain this distinction. The distinction in temperatures of burning of these substances is great and, apparently, it plays a decisive role.

Addition of small quantities of aluminum to ammonium salt of oxy acids, capable of intramolecular oxidation, very sharply increases the inclination of burning to transition to explosion[1], in spite of the fact that the speed of normal burning of these salts from the addition of aluminum is not increased. The influence of aluminum in the given case is concluded obviously in the increase of temperature of products of burning on its initial stage — the hotter the gases penetrating into the powder, the easier its particles ignite.

It is interesting that a clear parallelism is observed between the inclination of burning to transition to detonation and the detonational ability of a powdery explosive. Apparently, penetration of gaseous products of burning into the depth of the charge plays an essential role not only in the appearance of detonation, but also with its stationary propagation.

The Value of Dimensions of Particles of Powder Explosives and Certain Other Factors In the Penetration of Burning Into the Depth of a Charge

The role of magnitude of burning of a surface as a factor, determining the speed of gas formation, does not require explanations. In order to ensure the highest speed of gas formation from a unit of volume of the charge it is desirable that the explosive particles are very small. However, then penetration of gases into

[1] Detonational ability is increased also — critical diameter of detonation is greatly decreased.

the depth of the charge is hampered and, besides, they are more strongly cooled. All this interferes coverage by burning of the internal surface of the charge especially, if it is great. The most favorable for transition of burning to explosion is that case, when explosive particles are not too small, the gases penetrate deeply and their heat suffices in order to ignite the entire initial surface. After this as the surface was heated, the particles spontaneously are crushed by means of cracking, for example, as a result of thermal shock. Then both conditions are ensured, favoring acceleration: igniting the entire volume and the large surface of burning[1].

If the transformation quickly approaches the final products, then the surface of a solid explosive is in contact with gases of extraordinarily high temperature. This creates specially favorable conditions for increasing the surface of burning as a result of cracking of particles. It is possible that precisely such conditions are realized in the case of lead azide and explosives similar to it.

It is possible to imagine also a negative influence of cracking on the development of the process. If it occurs too easily and quickly during penetration into a charge of the first portions of weakly heated gases, then the dimensions of the particles and pores are decreased which can hamper further penetration of gases. Along with this the cracking, leading to baring of a great surface, can lead to too strong cooling of gases with corresponding consequences.

One should note one circumstance, complicating "internal" igniting in the case of small particles. Gas-penetrability of powder in this case is small, pressure of gases will be levelled in the thickness of the substance slowly, a pressure gradient will appear, under the influence of which the powder can be packed. This

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[1] Increase of surface as a result of cracking was observed in experiments at low and moderately increased pressures. Large pressures are able, in compressing the particles, to prevent divergence of the fragments formed during cracking and thus hamper growth of effective surface of burning.

packing will be expressed more strongly, (at a given gas-penetrability) the less density of the substance, the easier it is packed, the larger and the faster grows the pressure of the products of burning of the igniter.

Let us consider still certain phenomena, appearing in the wide-spread method of igniting of a powdery charge [1] in a closed or semi-closed vessel, significantly complicating the picture.

Hot gases of the igniter[2] arrive in contact with the open end of the charge and heat the explosive from the surface. In further development of the process, an essential influence is rendered by the relative density of the ignited substance. If the explosive is pressed to a great density, then the action of gases is limited by ignition of the charge from the surface. If its relative density is not so great, i. e., if between particles there are significant gaps, then the gases penetrate into the depth of the charge, heating with this particles of the explosive. The gases themselves, by measure of their deepening in the charge are naturally cooled. Corresponding to the different temperature of gases by depth of penetration also their action then on particles of the explosive, will be distinguished. Schematically it is possible to separate three zones from the external surface of the charge in depth.

In the first of them, nearest to the end of the charge, the gases are sufficiently hot in order to quickly ignite the particles from the surface. The particles ignite in this case after heating of a thin surface layer of the substance and burn with normal speed similar to how grains of powder burn in firing or in conventional experiments in a manometric cylinder.

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[1] The explosive is located in a case open on one end, made from a material which is incombustible in the given conditions, installed in a container.

[2] It is obvious that such a role can play products of burning of the actual explosive. If the igniter of gases will not form (for example, incandescent wire), then from the very beginning of burning, and if the igniter is gas type, then after a certain time, penetration of heat into the depth of the charge is accomplished by filtration of gaseous products of burning of the actual explosive.

In the second zone the gases are colder and warm-up of explosive particles occurs slower. Ignition occurs with a certain delay and to the moment of origination of burning the particles succeed in being heated completely or at least to a significant depth. In connection with this burning proceeds faster than if nonheated particles were burned, and the speed of gas formation is higher than at normal for given initial temperature and pressure of the burning rate on the same surface. Here a case is also possible, when a particle to the moment of its ignition from the surface was heated to so high a temperature that in it occurs, along with burning from the surface a quick volume reaction. The total speed of transformation and gas formation in this case will be the highest.

Finally, in the third zone gases were cooled so much that they no longer in a state to ignite particles from the surface. However, these gases can warm the explosive so much that at a sufficient thickness of heated layer in it with a corresponding delay will appear a thermal explosion. If the explosive melted, then burn-up can lead to melting and agglomeration of particles, leading to a decrease of the internal surface. These phenomena are especially essential in the case of an explosive with a low temperature of melting. If, however, the charge is melted completely or in general a sufficiently thick layer of liquid is formed, then transition from solid to liquid state can be done possibly with new ways of acceleration of burning. It is known that for certain liquid explosives (for example, nitroglycerine, nitroglycol) igniting in a closed container easily leads to explosion.

Conclusions

The principal analogy between the possibility of acceleration of a homogeneous exothermal transformation in an explosive charge and burning of this charge on the internal surface is considered. On this basis the most important conditions determining the possibility of transition to explosion of burning of solid explosives, in the first place powder types, were established.

Tape No. MT-63-254

Chapter 4 Article No. 38

Pages 540-542

IV. VARIOUS INVESTIGATIONS

A. A. Shidlovskiy

38. Water as an Oxidizer in Reactions With Inorganic Substances

It is well-known that water represents a very durable chemical compound: the heat of formation of liquid water equals 68.32 kcal/g-mole and of water vapor, 57.80 kcal/g-mole. It is known also that exothermal reactions of water with active (alkaline or alkali earth) metals proceed easily even at room temperature. Earlier we established [3], [4] that in conditions of high temperature and pressure the reaction of interaction of water with such metals as magnesium or aluminum can proceed in the form of burning or explosion.

$$\overbrace{nMe+mH_2O}^{2me}=Me_nO_m+mH_2 \qquad (1)$$

Water with this executes the role of the oxidizer -- the receiver of electrons. But oxidizing properties of water can be developed in other reactions: during its interaction with nonmetals possessing noticeably expressed reducing properties, and also with the lowest oxides of certain metals.

Highly exothermal effects accompany the reaction of interaction of water with boron and silicon[1].

$$3H_2O_{liq}+2B_{crys}=B_2O_{3\,crys}+3H_2+97\ \text{kcal} \qquad (2)$$
$$2H_2O_{liq}+Si_{crys}=SiO_{2\,crys}+2H_2+[illegible]\ \text{kcal} \qquad (3)$$

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[1] Heat of reactions in all cases was calculated by us on the basis of data on ΔH_{298} of reference book [6]. During the course of reactions (2) and (3) hydrides of boron or silicon can be formed side by side with hydrogen.

Reaction (2) proceeds only at temperature of red incandescence, reaction (3) also at room temperature, if in the water there is a certain quantity of alkali [2].

Interaction of water with phosphorous, expressed by equation

$$5H_2O_{liq} + 2P_{wh} = P_2O_{5\,cry} + 5H_2 + 18\ \text{kcal} \qquad (4)$$

would be accompanied by the emission of a comparatively small quantity of heat (q = 118 kcal per kg of mixture of reacting substances).

It is known that at ordinary conditions the system (H_2O + P) is sufficiently chemically stable. However, the course of the secondary exothermal reaction

$$P_2O_{5\,cry} + 3H_2O_{liq} = 2H_3PO_{4\,crys} + 47\ \text{kcal} \qquad (5)$$

gives additional heat and in connection with this the reaction ability of the system (H_2O + P) is increased.

As is known, the reaction

$$4H_2O_{liq} + P_{wh} = H_3PO_{4\,crys} + 2.5H_2 + 33\ \text{kcal} \qquad (6)$$

(q = 320 kcal/kg) has found in truth comparatively recently, industrial application [1].

The interaction of water with carbon is an endothermic process:

$$H_2O_{vap} + C_{graphite} = CO + H_2 - 31\ \text{kcal} \qquad (7)$$

and therefore practically is realized only at high temperatures. Also endothermic and therefore more difficult to realize would be processes of interaction of water with nonmetals: As, S_2 Se, and Te -- for example,

$$3H_2O_{vap} + 2As_{crys} = As_2O_{3\,crys} + 3H_2 - 16\ \text{kcal} \qquad (8)$$

Our calculations show that the reaction of oxidation by water (liquid) of the lowest oxides of certain metals can proceed with heat liberation; for example,

$$SnO_{crys} + H_2O_{liq} = SnO_{2\,crys} + H_2 + 2\text{ kcal} \qquad (9)$$

$$Nb_2O_{4\,crys} + H_2O_{liq} = Nb_2O_{5\,crys} + H_2 + 7\text{ kcal} \qquad (10)$$

It is possible that the process of oxidation by water of germanium oxide (GeO) to the dioxide will also be exothermal; calculations here cannot be performed, since in thermochemical reference books do not contain value of ΔH for GeO_{crys}.

Passing to consideration of the interaction of water with the lowest oxides of nonmetals, we will indicate first of all the well-known reaction

$$CO_{gas} + H_2O_{vap} = CO_{2\,gas} + H_2 + 9\text{ kcal} \qquad (11)$$

Especially important is the oxidation of sulfur dioxide. The reaction

$$H_2O_{liq} + SO_{2\,gas} = SO_{3\,crys} + H_2 - 29\text{ kcal} \qquad (12)$$

is endothermic, as is the reaction

$$H_2O_{vap} + SO_{2\,gas} = SO_{3\,crys} + H_2 - 18\text{ kcal} \qquad (13)$$

However, the secondary exothermal reaction

$$SO_{3\,crys} + H_2O_{vap} = H_2SO_{4\,liq} + 26\text{ kcal} \qquad (14)$$

leads to the fact that the interaction SO_2 with a surplus of water vapor is an exothermal and therefore more easily realizable process:

$$2H_2O_{vap} + SO_{2\,gas} = H_2SO_{4\,liq} + H_2 + 8\text{ kcal} \qquad (15)$$

Heat, emanating during the hydration of sulphuric acid by a surplus of water vapor, should still increase the exothermic nature of this reaction.

At the same time one can hardly trust to obtain hydrogen as a result of the interaction of sulfur dioxide with water vapor, since H_2 will reduce the surplus SO_2, turning it to sulfur:

$$2H_2 + SO_2 = 2H_2O_{vap} + S_{cryst} + 45 \text{ kcal} \qquad (16)$$

and, consequently, the total reaction between water vapor and sulfur dioxide will be expressed by the equation

$$2H_2O_{vap} + 3SO_{2\,gas} = 2H_2SO_{4\,liq} + S_{cryst} + 50 \text{ kcal} \qquad (17)$$

According to Barnet and Wilson [5], this (in their words) complicated and little intelligible reaction of disproportionation proceeds at 150°. We propose that the mechanism of this reaction can be explained by the consecutive flow of reactions (15) and (16).

One should note also that water vapor can play the role of oxidizer also in reference to other classes of chemical compounds, for example, the hydrides of many metals and certain nonmetals (SiH_4; PH_3), the borides and silicides of many metals, etc.

From the above it appears that water can, especially at increased temperatures, take a very active part in very different chemical reactions between inorganic substances. It is possible that the most exothermic of the reactions described above -- for example, reactions (2) and (3) --with selection of the proper conditions of temperature and pressure can be realized in the form of processes of burning or explosion.

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Tape No. MT-63-254

Chapter 4 Article 39

Pages 543-545

A. A. Shidlovskiy

39. Broadening of Region of Application of the Thermochemical Law of Constant Differences Precomputation of Unknown Heat of Formation of Salts of Ammonium

In the work of A. F. Kapustinskiy and our [4] is shown the possibility of application of the thermochemical law of constant differences for approximate calculation of the heat of formation of solid inorganic compounds.

Continuing this work, we compared in pairs the heat of formation 27 pairs of crystalline salts of potassium and ammonium. Corresponding data of this comparison are given in Table 1. The heat of formation of the majority of salts we took from reference book [6]; for salts with anions $S_2O_5^{2-}$; SO_4^{2-}. $MgSO_4 \cdot 6H_2O$ and $[Fe(CN_6]^{4-} \cdot 3H_2O$ — from reference book [1]; for iodate of ammonium the value of the heat of formation was found experimentally [4]. Data on the heat of formation of aqueous solutions were taken for dilution ∞, or if there were no such data, for maximum dilution. As can be seen from Table 1, the mean deviation from the difference of 28.4 kcal for crystalline salts of potassium and ammonium constituted ±2 kcal/g-equiv. These deviations are distributed by magnitude as follows.

Deviation in kcal	Number of comparisons
from 0 to 1	10
from 1 to 2	4
from 2 to 3	8
from 3 to 4	3
from 4 to 6	2

The greatest values of deviation are given by anions:

F^-—5.5 kcal; ClO_4^-+5.8 kcal.

Since for aqueous solutions of salts of potassium and ammonium the mean difference in the heat of formations constitutes 28.4±0.3 kcal (see Table 1) and the greatest deviation does not exceed ±0.9 kcal, it is evident that the significant deviations for the ions F^- and ClO_4^- are connected with differences in the heats of dissolution of salts of potassium and ammonium.

Actually, as can be seen from the data given below, the heats of dissolution of these salts are not equal ($-\Delta$ H of solution kcal/g-equiv).

	K^+	NH_4^+	difference(Δ)
F^-	+4,2	−1,2	+5,4
ClO_4^-	−12,2	−6,3	−5,9.

Deviations from the difference (28.4) and differences in the heats of dissolution (Δ) fully counteract each other.

Ascertaining of causes of differences in the heats of dissolution of salts of potassium and ammonium requires further theoretical and experimental work.

Using the difference $K^+ - NH_4^+ = 28.4$ kcal/g-equiv, we calculated approximately heats of formation unknown to this time for certain well-studied salts of ammonium, whose properties and methods of obtaining are described in the literature [5].

Results of these calculations are given in Table 2.

The limits of deflection shown in the last column on the right of Table 2 do not exceed 1.5—2.0% of the magnitude of the heat of formation of the considered salts.

Using the constant difference $Na^+ - NH_4^+$, equal to 22.6 kcal/g-equiv [4], we obtained the data in Table 2 B.

The precomputations for salts of ammonium, made by the differences $K^+ - NH_4^+$ and $Na^+ - NH_4^+$, are near one to another.

In conclusion we will show that in the present handbook [6] there are clearly incorrect values of $\Delta H = -598$ for $K_2Cr_2O_7 \cdot CrO_3 (K_2Cr_3O_{10})$.

For trichromate of ammonium $(NH_4)_2Cr_3O_{10}$ we obtain by experimental means the value $-\Delta H_{298} = 580 \pm 6$ kcal/g-mole [3].

Table 1

Difference in the heats of formation ($-\Delta H_{298}$) of crystalline salts of potassium and ammonium and their aqueous solutions.

1) № по пор.	2) Анионы	3) Кристаллические соли				4) Водные растворы солей			
		K^+	NH_4^+	5) ΔH K^+—NH_4^+ ккал/г-экв	Отклонение от разности 28,4 6)	K^+	NH_4^+	5) ΔH K^+—NH_4^+ ккал/г-экв	Отклонение от разности 28,4 6)
1	F^-	134,5	111,6	22,9	—5,5	138,7	110,4	28,3	—0,1
2	Cl^-	104,2	75,4	28,8	+0,4	101,1	71,8	29,3	+0,9
3	Br^-	93,7	64,6	29,1	+0,7	88,9	60,7	28,2	—0,2
4	J^-	78,3	48,3	30,0	+1,6	73,4	45,1	28,3	—0,1
5	ClO_4^-	103,6	69,4	34,2	+5,8	91,4	63,1	28,3	—0,1
6	JO_3^-	121,5	94,0	27,5	—0,9	115,0	86,4	28,6	+0,2
7	NO_2^-	88,5	63,1	25,4	—3,0	85,2	57,1	28,1	—0,3
8	NO_3^-	117,8	87,3	30,5	+2,1	109,4	81,1	28,3	—0,1
9	CN^-	26,9	0,0	26,9	—1,5	24,1	—4,6	28,7	+0,3
10	CNS^-	48,6	20	28,6	+0,2	42,8	14,5	28,3	—0,1
11	HSO_4^-	276,8	244,8	32,0	+3,6	274,3	245,9	28,4	0,0
12	HS^-	63,2	38,1	25,1	—3,3	64,1	35,1	29,0	+0,6
13	$H_2PO_4^-$	374,9	346,7	28,2	—0,2	370,4	342,9	27,5	—0,9
14	HCO_3^-	229,3	203,7	25,6	—2,8	224,5	196,9	27,6	—0,8
15	HCO_2^-	158	132,8	25,2	—3,2	157,7	129,8	27,9	—0,5
16	$CH_3CO_2^-$	173,2	147,8	25,4	—3,0	176,9	148,1	28,8	+0,4
17	SO_4^{2-}	342,7	281,9	30,4	+2,0	337,0	280,4	28,3	—0,1
18	SO_3^{2-}	266,9	212,0	27,4	—1,0	269,1	211,3	28,9	+0,5
19	$S_2O_5^{2-}$	361,1	299,6	30,7	+2,3	350,1	293,3	28,4	—0,0
20	$S_2O_8^{2-}$	458,3	396,4	31,0	+2,6	445,3	387,8	28,7	+0,3
21	CrO_4^{2-}	330,5	275,2	27,6	—0,8	326,0	269,4	28,3	—0,1
22	$Cr_2O_7^{2-}$	485,9	425,5	30,2	+1,8	468,7	412,6	28,0	—0,4
23	$PtCl_4^{2-}$	254,2	195,5	29,4	+1,0	242,8	186,9	27,9	—0,5
24	$C_2O_4^{2-}$	320,8	268,7	26,0	—2,4	317,1	260,6	28,2	—0,2
25	$SO_4^{2-}ZnSO_4 \cdot 6H_2O$	1011,8	955,6	28,1	—0,3	—	—	—	—
26	$SO_4^{2-}MgSO_4 \cdot 6H_2O$	1081,8	1024,4	28,7	+0,3	—	—	—	—
27	$[Fe(CN)_6]^{4-} \cdot 3H_2O$	340,3	216,1	31,1	+2,7	119,5	4,2	28,8	+0,4

7) Средняя разность 28,4 ккал
8) Среднее отклонение ±2 ккал

7) Средняя разность 28,4 ккал
9) Среднее отклонение ±0,3 ккал

1) No. of pairs; 2) Anions; 3) Crystalline salts; 4) Aqueous solutions of salts; 5) kcal/g-equiv; 6) Deviation from the difference 28.4; 7) Mean difference 28.4 kcal; 8) Mean deviation ± 2 kcal; 9) Mean deviation ± 0.3 kcal.

Table 2

Heats of formation of crystalline salts of ammonium (in kcal/g-mole)

A. Constant difference $K^+ - NH_4^+ = 28.4$ kcal/g-equiv.

1) Анион	2) $-\Delta H_{298}$ солей калия ккал/г-моль [6]	Вычисленная $-\Delta H_{298}$ солей аммония, в ккал/г-моль 3)
ReO_4^-	264,0	235,6±2
SeO_4^{2-}	266,9[2]	210,1±4
$SnCl_6^{2-}$	362,9	306,1±4
$PdCl_4^{2-}$	261,6	204,8±4
$PtCl_6^{2-}$	301,0	244,2±4
AlF_6^{3-}	777,6	692,4±6

1) Anion; 2) $-\Delta H_{298}$ of salts of potassium, kcal/g-mole; 3) Calculated $-\Delta H_{298}$ of salts of ammonium, in kcal/g-mole;

B. Constant difference $Na^+ - NH_4^+ = 22.6$ kcal/g-equiv.

Анион 1)	4) $-\Delta H_{298}$ солей натрия ккал/г-моль [6]	Вычисленная $-\Delta H_{298}$ солей аммония в ккал/г-моль 3)
SeO_4^{2-}	258	212,8±4
AlF_6^{3-}	759,5	691,7±6

4) $-\Delta H_{298}$ of salts of sodium, kcal/g-mole.

Using the difference $K^+ - NH_4^+ = 28.4$ kcal, we obtain for $K_2Cr_3O_{10}$ the value:

$$\Delta H_{298} = -(580 \pm 6) - 28.4 \cdot 2 = -637 \pm 6 \text{ kcal/g-mole.}$$

Conclusions

1. On examples of salts of potassium and ammonium with identical anions, it was shown that the thermochemical law of constant differences can be used with success for the approximate calculation of the heat of formation of crystalline salts which have a common cation or anion, equal or close values of heat of dissolution, and also are strong electrolytes.

2. With accuracy ± 2% (± 2 kcal/g-equiv) we calculated the unknown heats of formation of the perrheniate, selenate, hexachlorostannate, tetrachloropalladiate, hexachloroplatinate, and hexafluoraluminate of ammonia.

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Tape No. MT-63-254 Chapter 4 Article 40

Pages 546 - 549

Yu. Ya. Maksimov

40. Vapor Pressure of Nitro Derivatives of Benzene

The data available in literature concerning vapor pressure of mono- and dinitrobenzene up to the boiling point [2], [3] do not cause any doubts, since the corresponding measurement was accomplished in an area of temperatures at which the stability of these compounds is quite high. Otherwise there is the matter with measurement of vapor pressure of trinitrobenzene which, as distinguished from the first two substances, decomposes with a marked speed even at a temperature below the boiling point. This circumstance obstructs the immediate determination of its boiling point. A. F. Belyayev [1], upon determining it by evaporating an explosive suspension in 2 mg from the surface of a heated metal block, gives an approximate value of 315°. The magnitude of latent heat of evaporation, which he found by the time of evaporating a suspension of this explosive at various temperatures is approximately 18.5 kcal/mole. However, an experimental check of the values of vapor pressure, calculated by the boiling point and heat of evaporation, found by A. F. Belyayev, indicated the divergence between the results of the experiments and his data. This served as the cause for a more detailed study of vapor pressure of trinitrobenzene.

For determination of vapor pressure of this substance at a variable temperature, a 0.05g suspension of it was heated in a thoroughly evacuated (up to 10^{-3} — 10^{-4} mm Hg) and sealed glass vessel equipped with a manometer of the Bourdon type. The temperature of the bath with weak tin and lead, in which the vessel was placed with the explosive being investigated, was maintained constant with an accuracy of ±0.5°.

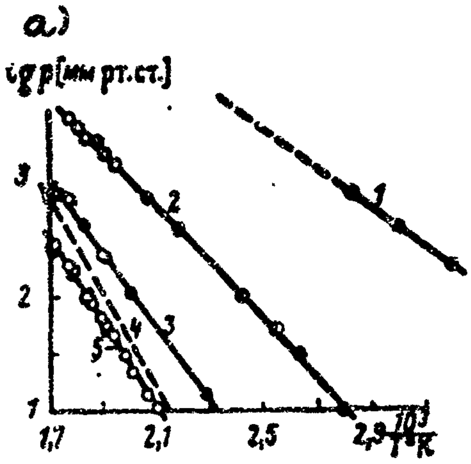

Fig. 1. Temperature dependence of pressure of saturated vapor for substances of the benzene-trinitrobenzene series.
1 — Benzene, 2 — mononitrobenzene, 3 — dinitrobenzene, 4 — trinitrobenzene (according to data of A. F. Belyayev) and 5 — trinitrobenzene (according to our data).
a) mm Hg

Vapor pressure was also measured for mono- and dinitro- derivatives of benzene. The measurements were conducted with one sample of the substance with a sequence increase of temperature. A specially set-up experiment with dinitrobenzene showed that for heating a vessel containing the substance from room temperature to 250°, 2 — 3 minutes are required. Before measurement, at each temperature, exposure of 5 — 10 minutes was accomplished. The results of the experiments are given in Table 1 and Figure 1. The data obtained on the applied method well corresponds with what is available in literature.

Measurement vapor pressure of trinitrobenzene at a temperature of 200 — 250° was conducted with one sample and the degree of filling the vessel with the substance was 10^{-3}g/cm^3 [1]. The reliability of the measurements made in this experiment is confirmed by the fact that the pressure in the vessel, measured at room temperature after the experiment, was less than 1 mm Hg. Upon raising the

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[1] During the study of thermal disintegration of trinitrobenzene it was established that the speed of its decomposition in liquid state is greater than in vapors. Therefore it was desirable to select a low degree of filling of the vessel so that the quantity of the substance in liquid phase is minimum.

temperature to 270° and higher the speed of decomposition of trinitrobenzene was increased so much, that after the time necessary for one measurement, a marked quantity of gases is formed, and therefore determination of vapor pressure of the explosive becomes not very reliable. For the purpose of excluding the influence of decomposition, for each determination a new portion of the substance was selected, and vapor pressure was determined by means of extrapolating the pressure building up in the vessel during decomposition, at a time equal to the time of heating. From Fig. 2, in which curves of the growth of pressure are depicted with time in the case of heating of trinitrobenzene at 312°, one can see that the reproducibility of the data in determining vapor pressure under these conditions is completely satisfactory.

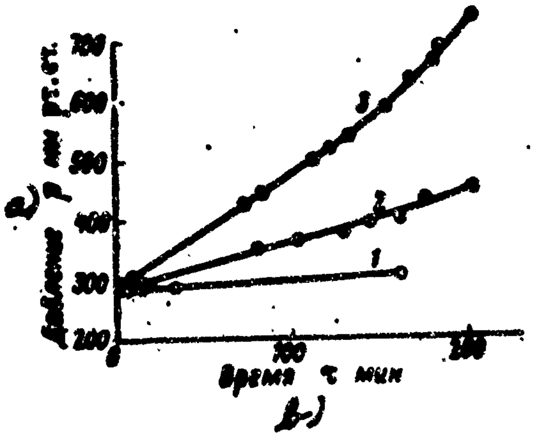

Fig. 2. Growth of pressure in time in the case of decomposition of trinitrobenzene at 312° and various degrees of filling of the reaction vessel (in g/cm^3·10^4):
1 — 18.1, 2 — 37.1, 3 — 81.8.
a) Pressure p mm Hg; b) Time τ minutes.

The obtained results of measuring pressure of saturated trinitrobenzene vapor are given in Table 1, and the corresponding points are plotted on the graph log p-1/T (Fig. 1). For a comparison on this graph is depicted a line 4, constructed according to A. F. Belyayev's data. From Fig. 1 it is clear that in the whole studied range of temperatures, the values of vapor pressure of trinitrobenzene, obtained by us are lower than those calculated by Belyayev. The boiling point, determined by extrapolation of the obtained data at a

Table 1

Vapor pressure of nitro-derivatives of benzene at variable temperature

1- Вещество	2 Температура °C	3 Давление насыщенного пара *мм* рт. ст.	$\frac{1}{T°K}\cdot 10^3$	lg *p*
4-Нитробензол	239	1430	1,95	3,156
	250	1775	1,91	3,250
	259	2167	1,88	3,360
	269	2512	1,84	3,400
	280	3022	1,81	3,481
	291	3582	1,78	3,551
5-1, 3-динитробензол	252	220	1,91	2,343
	253	230	1,90	2,362
	290	687	1,78	2,837
	291,5	716	1,77	2,856
6-1, 3, 5-тринитробензол	202,5	11	2,10	1,042
	210,5	14	2,07	1,146
	223,5	22	2,01	1,342
	234,5	31	1,98	1,492
	245,5	46	1,94	1,663
	250	56	1,91	1,748
	250	52	1,91	1,716
	256	64,5	1,89	1,810
	267	89	1,85	1,949
	271	100	1,84	2,000
	271	101	1,84	2,004
	271	102	1,84	2,009
	286	165	1,79	2,218
	286	166	1,79	2,220
	292	184	1,77	2,265
	312	287	1,71	2,458
	312	285	1,71	2,455
	312	293	1,71	2,467

1)
3)
6)
to

1) Substance; 2) Temperature; 3) Pressure of saturated vapor mm Hg; 4) Nitrobenzene; 5) 1,3-dinitrobenzene; 6) trinitrobenzene.

Table 2

Magnitudes characterizing boiling of nitro derivatives of benzene

	1 Вещество	lg A	Скрытая теплота испарения при $T_{кип}$ λ 2 кал/моль	Температура кипения при 760 мм рт. ст. 3 °C	4 Отношение Трутона $\frac{\lambda}{T_{кип}}$
5-	Бензол	7,44	7 350	80,1	20,8
6-	Мононитробензол	8,03	11 600	210,5	23,8
7-	1, 3-динитробензол	8,56	14 500	300	25,3
8-	1, 3, 5-тринитробензол	9,05	17 500	350	28,1
9-	по нашим данным				
10-	по данным Беляева	—	18 500	315	31,5

1) Substance; 2) Latent heat of evaporation a T boil λ cal/mole; 3) Boiling point at 760 mm Hg, °C 4) Truton's ratio, $\frac{\lambda}{T\ boil}$; 5) Benzene; 6) Mononitrobenzene; 7) Dinitrobenzene; 8) Trinitrobenzene; 9) According to our own data; 10) According to Belyayev's data.

Note. Values of lg A are given for p in mm Hg.

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pressure of 760 mm Hg, constitutes 350°, which is 35° above the value found by A. F. Belyayev. This distinction is stipulated, probably, by the fact that in our experiments upon measuring vapor pressure the part of the decomposition factor was reduced to minumum at the time when in A. F. Belyayev's work the calculation of this factor was extremely difficult.

Joint consideration of the dependence $p=f(T)$ for substances of the series benzene-trinitrobenzene (Fig. 1) also is in favor reliability of the results obtained.

Temperature dependence of vapor pressure of the nitro compounds under consideration near the boiling point can be expressed by the equation

$$p = A \cdot e^{-\frac{\lambda}{RT}}.$$

Coefficients of the equation, boiling point and Truton's ratio for the four substances we are interested in are in Table 2. From the data of this table, it is evident that the magnitude of Truton's ratio, equal for benzene 20.8, upon sequence introduction of it into a molecule of the NO_2 group grows regularly, reaching for trinitrobenzene the value of 28 -- 30, which one and a half times exceeds the normal value of this ratio (21.0). A similar regularity was first observed by A. F. Belyayev [1] in an example of nitric acid esters of aliphatic alcohol and has, probably, a common character for organic compounds contained in a NO_2-group molecule. In connection with this, it should be said that the previous opinion among certain investigators concerning the invariability of the normal value of Truton's ratio for compounds of this type, evidently, is erroneous.

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Tape No. MT-63-254

Chapter 4 Article 41

Pages 550-557

I. F. Blinov (Deceased), L. M. Svetlova

41. Influence of Shell on the Detonation Ability of Certain Dinitro Compounds of the Benzine Series[1]

The presence of a shell has a great influence on the detonation ability of an explosive. It retards the radical scattering of the exploding substance and consequently, in accordance with the principle of Yu. B. Khariton [4], it lessens the critical diameter of the charge. Precisely because of this a substance which is not capable of stable detonation at a given change diameter in the absence of a shell becomes readily detonatable at the same diameter with a shell.

A strong shell which does not burst during explosion will reduce the initial diameter of the change especially strongly.

Investigating the detonation of ammonium-saltpeter mixtures, A. F. Belyayev came to the conclusion [1] that owing to the extremely small time of the course of the explosive process, the action of a shell is determined basically by its inertial resistance (mass). However, a shell of loose material shows a lesser effect on the stability of detonation than does a shell of equal mass from strong materials, creating additional resistance to the escape of the unreacted explosive.

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[1] This work was carried out under the leadership of I. F. Blinov, who was prevented by an untimely death from completing it. The author of the article expressed her deep gratitude to A. I. Gol'binder for his help in preparing the manuscript and his valuable advice in discussion of the results.

A. F. Belyayev indicates also that an increase in the diametric dimension of the change is equivalent to surrounding a charge of lesser diameter with a loose inert shell of equal mass.

The influence of the properties of the shell on the possibility and rate of propagation of detonation appears in the case when the explosive charge has a diameter far from the limit corresponding to the maximum rate of detonation. The study of the influence of the shell on detonation ability is therefore significant for those explosives which have a sufficiently great critical charge diameter and for which is observed a significant difference between the critical and limit diameters. The number of such systems includes, together with mixtures which for the most part have been studied from this point of view, substances which possess low explosivity -- in particular, aromatic dinitro compounds. One would expect that the study of such compounds will provide a fuller and more graphic presentation of the influence of various characteristics of shells (density, strength, compressibility) on the detonation ability of charges. Together with this, the study of the influence of shells on the detonation ability of such compounds has significant practical interest for the evaluation of the actual danger of explosion in the various conditions of their production, storage, and application.

In connection with this, in a number of other works on the study of the explosive properties of dinitro compounds [2], [3] there was conducted an investigation on the clarification of the effect of a shell on the detonation ability of these substances. The results of this investigation are given below.

Experimental Part

Experiments were conducted with technical products of factory manufacture. As objects of investigation we used the following:

dinitrophenol, melting temperature..........................114.5°

dinitrotoluene,melting temperature.......................... 63.5°

dinitrochlorobenzene, melting temperature..............50.0°

dinitroaniline, melting temperature.... ....178.0°

dinitronaphthalene, melting temperature ....155.0°

Earlier [2] it was established that the critical diameter for detonation of charges of similar explosives increases with growth of their density. In connection with this, in the present work we used charges in the form of powder, with a density close to the fill density of the corresponding substance. All experiments were conducted with crystalline products passing 100% through a screeen with 11 holes per cm.

We tested shells of various strengths, densities, and compressibilities: steel pipes, tubes rolled from sheet lead and iron, glass and ceramic tubes, shells constituted of separate steel strips, shells of liquid, friable (sand) and plastic materials.

In experiments with shells of liquid, clay, or sand the charge of the tested substance, in a casing of paraffined paper, was placed in a casing of greater diameter; the free space between the walls was filled with liquid, plastic clay, or dry sand.

In the period of carrying out the given work we were not able to measure the detonation rate. The results of the experiments were evaluated by the deformation of a lead cylinder on which we exploded the test charges in the various shells. The experimental procedure was analogous to the standard test for brisance.

In order to judge more completely the stability of explosion we applied lengthening of the charge; in most of the experiments the charge length was 100 mm (diameter 2.5 - 3.5), and in some experiments we used charges 200 mm in length. Detonation of the test charges was triggered by No. 8 detonating caps. Experiments with dinitronaphtholene were an exception; there we used intermediate detonators of pressed tetryl, 5 to 10 g in weight.

In evaluating the results of the experiments it is necessary to consider that the presence of the shell influences them in a twofold way. On the one hand, by impeding the scattering of the detonation products, the shell lessens the "chemical" losses, in connection with which the completeness of the transformation of the initial explosive into detonation products grows and the detonation rate is increased. On the other hand, by delaying the radical scattering, the shell strengthens the mechanical action of the explosion products on the lead cylinder. This latter effect of the shell will tell further when the test charges is an explosive for which the applied diameter is greater than the limit and the completeness of transformation and, consequently, the detonation rate are changed because of the presence of the shell.

The method we used to conduct the experiments did not permit the separation of the two indicated factors. Besides this, we tested charges of different diameters. A change in charge diameter and the presence and quality of a shell can have a mutual effect on the pressing of the lead cylinder. In connection with this the results obtained permit reliable differention only of the cases of the presence or absence of explosion of the test charge, and do not give reliable data for evaluation of the completeness of transformation and the detonation rate in each case.

In Table 1 are presented results of experiments with dinitrophenol at a charge density of 0.62 to 0.65 g/cm^3. Charges of this density in thin paper casings will detonate at a diameter of 40-45 mm; in some experiments at a charge diameter of 40 mm attenuation of detonation was observed.

In Table 2 are shown the results of experiments with dinitrotoluene at a charge density of 0.6 and 0.8 g/cm^3. Dinitrotoluene at a density of 0.6 g/cm^3 was tested in paper or cardboard cases. The critical diameter in these conditions was about 45mm.

Table 1

Influence of sheal on detonation ability of dinitsophenol

1) Материал оболочки	2) Диаметр оболочки внутренний/наружный *мм*	3) Вес оболочки на 1 *см* длины заряда *г/см*	4) Обжатие свинцового цилиндра *мм*
5) Стальная цельнотянутая трубка	29/30,4	45	20,8
6) Свинцовая трубка	29/35	47	15,5
7) Вода	29/77	40	9,5
	29/101	83	7,5
8) Парафин	29/73	40	9,3
9) Песок	29/63	40	1,2
	29/79	41	1,3
10) Жестяная трубка	30/31	5,2	7,8
	30/32	8,4	10,4
11) Стальные полосы шириной 4—5 *мм*	35/43	38	20,3
			29,0
12) Свинцовая трубка	35/41	47	18,1
13) Керамиковая трубка	35/47	14	16,3
			17,5
7) Вода	35/76	40	14,7
9) Песок	35/56	40	15,5
			14,2
10) Жестяная трубка	35/36	3	12,9
14) То же	35/37	6	12,6

1) Shell material; 2) Shell diameter, internal/external, mm; 3) Weight of shell per cm of charge length, g/cm; 4) Pressing of lead cylinder, in mm; 5) Seamless steel pipe; 6) Lead pipe; 7) Water; 8) Paraffin; 9) Sand, 10) Tin pipe; 11) Steel strips 4-5 mm wide; 12) Lead pipe; 13) Ceramic pipe; 14) the same.

In Table 3 are given the results of experiments with dinitrochlorobenzene at a density of 0.8 - 0.85 g/cm^3.

Table 4 shows results of experiments with dinitroaniline at a charge density of 0.7 - 0.8 g/cm^3. Without a shell dinitroaniline will detonate at a diameter

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of 60 mm.

Dinitronaphthalene possesses a very low detonation ability. A charge 200 mm in diameter and 200 mm high in a paper shell with an intermediate detonator of pressed tetryl (wt. 100 g) will not detonate completely.

Table 2

Influence of shell on detonation ability of dinitrotoluene

1) Материал оболочки	2) Диаметр оболочки внутренний/наружный *мм*	3) Вес оболочки на 1 *см* длины заряда *г/см*	4) Обжатие свинцового цилиндра *мм*
5) Плотность зарядов 0,6 *г/см*³			
6) Стальная цельнотянутая трубка	40/50	57	26,0
7) Составная оболочка из стальных полос шириной 4—5 *мм*	40/48	42	20,0
8) Стальная трубка со швом	40/48	38	16,1
9) Стальная трубка со швом, разрезанная вдоль	40/48	38	12,8
10) Свинцовая трубка	40/44	30	21,3
11) Вода	40/80	40	15,0; 13,7
12) Глина	40/64	40	17,0; 14,6
13) Песок	40/70	40	2,4; 2,6
14) Жестяная трубка	40/41,2	3	15,2; 15,6
15) Стеклянная трубка	40/12,5	3,5	0,8
16) Плотность зарядов 0,8 *г/см*³			
8) Стальная трубка со швом	40/48	40	26,4
9) Стальная трубка со швом, разрезанная вдоль	40/48	40	25,0
10) Свинцовая трубка	40/46	40	26,0
11) Вода	40/80	40	1,2; 1,2
12) Глина	40/64	40	1,5
14) Жестяная трубка	40/41,2	7	1,0; 0,8

1-4) Same as Table 1; 5) Charge density 0.6 g/cm^3; 6) Seamless steel pipe; 7) Compound shell of steel strips 4-5 mm wide; 8) Steel pipe with seam; 9) Steel pipe with seam, slit along; 10) Lead pipe; 11) Water; 12) Clay; 13) Sand; 14) Tin tube; 15) Glass pipe; 16) Charge density 0.8 g/cm^3.

Table 3

Influence of shell on detonation ability of dinitrochlorobenzene

1) Материал оболочки	2) Диаметр оболочки внутренний/наружный *мм*	3) Вес оболочки на 1 *см* длины заряда *г/см*	4) Обжатие свинцового цилиндра *мм*
5) Жесть	40/41	3	17,5; 17,7
6) Стекло	40/42	3,2	11,0; 10,7
7) Бумага	40/48,8	—	0,4
8) То же	70/70,8	—	0,3
»	80/80,8	—	16,2

1) Material of shell; 2)Shell diameter, internal/external, mm; 3) Weight of shell per cm of charge length, g/cm; 4) Pressing of lead cylinder, mm; 5) Tin; 6) Glass; 7) Paper; 8) The same.

Table 4

Influence of shell on detonation ability of dinitroaniline

1) Материал оболочки	2) Диаметр оболочки внутренний/наружный *мм*	3) Вес оболочки на 1 *см* длины заряда *г/см*	4) Обжатие свинцового цилиндра *мм*
5) Стальная трубка	30/40,8	45	25,5
6) Стальная трубка, разрезанная вдоль на 2 части	30/40,6	45	12,4; 12,7
7) Стальные элементы в количестве 16 шт.	30/38	30	0,8; 1,3
8) Свинец	30/37,6	45	2,8; 2,5
9) Медь	14/23	12	Полная детонация в 2 опытах*

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10)* О результатах опыта судили по пробитию свинцовых пластинок.

1) Material of shell; 2) Shell diameter, internal/external, mm; 3) Weight of shell per cm of charge length, g/cm; 4) Pressing of lead cylinder, mm; 5) Steel pipe; 6) Steel pipe, cut along the length into 2 parts; 7) Steel elements in a quantity of 16 pieces; 8) Lead; 9) Copper; 10) The results of experiments can be judged by the penetration of the lead plates.

Table 5

Influence of shell on detonational ability of dinitronaphthalene

1) Материал оболочки	2) Диаметр оболочки внутренний/наружный *мм*	3) Вес оболочки на 1 *см* длины заряда *г/см*	4) Вес тетрилового детонатора *г*	5) Обжатие свинцового цилиндра *мм*
6) Стальная цельнотянутая трубка	40/50,8	45	5	18,7; 20,7
7) Стальная трубка со швом	40/48	40	5	8,3; 8,3
8) Составная оболочка из стальных полос, шириной 4—5 *мм*	40/50	40	5	4,7; 5,6
9) Свинцовая трубка	40/46	43	5	8,4; 8,4
6) Стальная цельнотянутая трубка	40/50	50	10	22,0; 24,2
7) Стальная трубка со швом	40/48	40	10	21,0; 19,5
8) Составная оболочка из стальных полос шириной 4—5 *мм*	40/48	42	10	8,0; 7,8
9) Свинцовая трубка	40/48	57	10	19,3; 20,6
6) Стальная цельнотянутая трубка	30/40,8	40	5	16,1; 16,0
10) Стальная цельнотянутая трубка, разрезанная вдоль	30/40	37	5	5,6; 3,5
8) Составная оболочка из стальных полос шириной 4—5 *мм*	30/43	48	5	0,8; 2,0
6) Стальная цельнотянутая трубка*	30/40	35	10	15,2
	30/40	37	11	18,1
10) Стальная цельнотянутая трубка, разрезанная вдоль	30/40	34	10	7,2
	30/40	37	10	12,4
11) Стальная цельнотянутая трубка из элементов*	30/40	30	10	0,8

12) * Применялись трубки длиной 200 *мм*.

1) Material of shell; 2) Shell diameter, internal/external, mm; 3) Weight of shell per cm of charge length, g/cm; 4) Weight of tetryl detonator, g; 5) Pressing of lead cylinder, mm; 6) Seamless steel pipe; 7) Steel pipe with seam; 8) Compound shell from steel strips, width 4-5 mm; 9) Lead pipe; 10) Seamless steel pipe, cut along; 11) Seamless steel pipe from elements; 12) Pipes 200 mm in length were applied

Since dinitronaphthalene detonates only from an intermediate detonator, we conducted control experiments with an inert substance (urotropine); pressing of lead cylinders in these experiments occurred as a result of detonation of the tetryl charge. With damage of the inert substance by a 10-gram tetryl charge in a pipe 40 mm in diameter and 100 mm in height we obtained pressing of the lead cylinder of 9.0 mm, and in a pipe of the same diameter, but 200 mm in length, of 7-8 mm. A tetryl charge of 5 g in these conditions gives pressing of lead columns of 4 and 1-2 mm, respectively. In Table 5 are shown results of experiments with dinitronaphthalene at a density of 0.45-0.60 g/cm^3.

Discussion of Results

On the example of the studied dinitroformations it is once again confirmed that the presence of a shell, rendering resistance to the scattering of the explosive makes possible detonation of a charge such a diameter, that without a shell detonation dies out. The most characteristic in this respect were experiments with dinitronaphthalene. While in a paper case this substance does not detonate even at a charge diameter of 200 mm, in a steel pipe its detonation occurs at a diameter of 30 mm.

Analysis of the results obtained allows to estimate the influence rendered by different characteristics of the shell on the detonation ability of the charge. Besides the inertial resistance of the shell, its strength has a clearly developed role. As in experiments with dinitrophenol (Table 1) a shell of tin, light but possessing essential tensile strength, assures the detonation of a charge of the same diameter at which explosion dies out in the case of an unbound but more massive shell of sand. Analogous results were observed in the case of dinitrotoluene (Table 2), where a charge with a density of 0.6 g/cm^3 detonated in a strong shell of tin and was not exploded in a glass shell of equal mass. In the case of a dinitronaphthalene charge 30 mm in diameter we observed complete detonation in a steel pipe and attenuation during explosion in a shell of the same material, but composed of separate strips and therefore devoid of strength (see Table 5).

It is possible to note that side by side with the inertial resistance and

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strength of the shell as a whole, an essential influence is exerted on the possibility of propagation of detonation also by the compressibility of the material -- its ability to be compacted under the action of explosion. As in the case of dinitrophenol (Table 1) a poorly compressible shell of water or paraffin assures detonation of a charge 29 mm in diameter, while in an easily compacted shell of sand the explosion of a charge of such diameter dies out In comparing these experiments one should consider that the average density and, consequently, inertial resistance of the shell as whole and greater in the case of sand than for water, but under fast actions water, apparently, possesses, as distinguished from sand, a certain resistance to bursting. Such a picture is obtained in experiments with charges of dinitrotoluene at a density of 0.6 g/cm^3 in shells of water or clay, on the one hand, and of sand on the other. From the considered point of view the results obtained with dinitrochlorobenzene are interesting. A charge of this substance, surrounded by a light and comparatively unstable, but poorly compressible shell of glass, detonates at a diameter of 40 mm. If such a charge is surrounded by an easily compacted shell of the same dinitrochlorobenzene 15 mm in thickness with a general mass 6-7 times greater than that of the glass shell, then detonation in charge, whose diameter is increased to 70 mm, dies out.

Experiments with charges of dinitrotoluene of various densities once again (see Table 2) confirmed that the critical diameter of propagation of detonation in it grows with an increase in density, as this was observed earlier for mixed explosives for example, ammonite.

The results obtained further that all the investigated dinitro compounds have detonation ability when in the form of a powdery charge of low density in a relatively strong shell and at small diameter. The greatest danger from this from this point of view is presented by dinitrophenol, dinitrotoluene and dinitrochlorobenzene. These results should be considered in examining questions of the danger of explosion in the production and application of compounds of this type.

Conclusions

1. The influence was studied of shells of various character on the brisance of explosion of certain dinitro compounds of the benzene series.

2. It was established that the less is the detonation ability of a substance, the greater is the influence exerted on the stability of detonation by the shell.

3. It was shown that besides the inertial resistance of the shell, its strength exerts a great influence on the detonation ability of the investigated substances.

It is possible to note also that together with inertial resistance and strength of the shell, its compressibility — ability to be compacted under the action of explosion — exerts an essential influence on the possibility of propagation of detonation.

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Tape No. MT-63-254

Chapter 4 Article 42

Pages 558-560

I. F. Blinov and L. M. Svetlova

42. On the Influence of the Dimensions of the Focus of Initiation on the Detonation Ability of Lowly-Sensitive Explosives

During the study of explosiveness of dinitro compounds an original and interesting phenomenon was detected, contradicting, on first look, the known data on the influence of the diameter of a charge on the possibility of propagation of detonation. Powder charges of low density at excitation of detonation by one and the same initiator stably detonated at small diameter of charge, at the time when in analogous charges of large diameter the detonation dies out.

Results of experiments, conducted for study of this phenomenon, are discussed below.

Experimental Part

The methodology of the experiments was very simple: from the investigated substances we prepared in different covers charges, having a density near being filled. As a rule, we used charges, the length of which equaled 3-4 diameters. Explosion was initiated by a percussion cap No. 8. In separate experiments we also used intermediate detonators in the form of filled or pressed charges made from powerful explosives (TEN, hexogene). The results of the experiment were judged by the deformation of the shell of charges, by imprint on a metallic plate which is in contact with the charge, or by compression of a lead cylinder, in which the tested charge was placed. At completion of this work we did not have the possibility to determine the speed of detonation. As the object of the investigation we used commerical products of in the form of crystal powder, sifted through a sieve with 11 apertures per cm.

In the described conditions 2.4 - dinitrotoluene with a density of charge of 0.5-0.65 g/cm^3 at initiation by a percussion cap-detonator stably detonates in a steel pipe with an internal diameter of 31 mm (length of charge 100 mm). In those same conditions, in a pipe 104 mm in diameter was observed attenuation of detonation with scattering of a large part of the substance.

The same results were received in testing dinitroaniline and picramic acid. These substances in charges with a density of 0.41-0.70 g/cm^3 stably detonate in a copper tube with an internal diameter of approximately 14 mm (thickness of wall 1-2 mm) and in a lead pipe 10 mm in diameter with a wall thickness of 2 mm at initiation by percussion cap-detonator. In steel pipes 40 mm in diameter in analogous conditions stable detonation is not observed.

Experiments with these substances were set up also according to the diagram shown in Fig. 1. Charges in narrow copper (d = 10 - 15 mm) and wide steel (d = 40 mm) pipes had identical density, which in various experiments with dinitroaniline changed from 0.64 to 0.82 and with picramic acid from 0.41 to 0.70 g/cm^3. In separate experiments the narrow pipe only touched the charge in the wide pipe, in others -- it was plunged into it at a depth from 1 to 5 cm. In all experiments detonation was spread in the pipe of smaller diameter and died out during transition to the wider pipe. The substance in the wide pipe, was partially scattered, and part of it was left in the form of a strongly consolidated layer on the walls of the pipe. In separate experiments where determination of the density of the remainder was made, it was equal to 1.33-1.43 g/cm^3. Results of experiments did not change in a case, when the wide part of the pipe was equipped with a screw-on cover.

It is essential to note that the observed attenuation of explosion in charges of large diameter is combined not with the impossibility of propagation of detonation in the given experiments, but with the conditions of initiation. Thus, in a case when we used intermediate detonators made of TEN or hexogene, if only in the form of filled charges, detonation of dinitro compounds in pipes of large diameter was spread stably, if only the diameter of these detonators exceeded

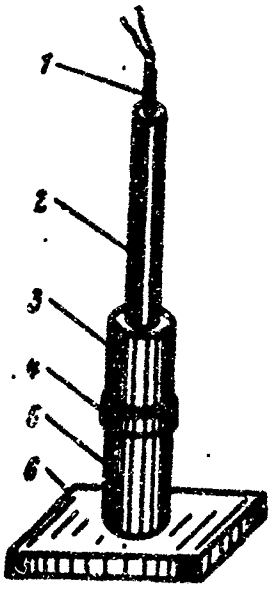

Fig. 1. Diagram of experiments with dinitroaniline and picramic acid. 1) percussion cap-detonator; 2) copper pipe with explosive; 3) steel pipe with explosive; 4) steel plate; 5) lead cylinder; 6) steel slab.

a certain minimum. Moreover, stable detonation can be observed in charges of large diameter also when it is excited by charges of the same dinitro compound of smaller diameter, if transition from small to large diameter was not abrupt. Corresponding experiments were conducted with dinitroaniline and picramic acid in conical charges. The investigated substance was poured into a shell made from sheet lead 2 mm thick, having the form of a truncated cone with the diameter of the smaller base 10 and larger — 45 mm (height of charge 135 mm). Explosion was excited by percussion cap-detonator. At initiation from the side of the smaller base full detonation occurred, and from the side of the larger — failure.

An original influence on the explosive ability of the investigated charges is rendered by density. Earlier it was established [2], what with its increase the detonational ability of dinitro compounds is lowered (critical diameter grows). At the same time, upon lowering of density, failures are observed with those methods of initiation, that ensure explosion of charges of large density. Thus, in the described experiments with picramic acid in cones with a shell made from lead full explosion was observed with initiation from a large base by percussion cap-detonator of a charge with a density of 0.65 g/cm^3 and failure at a density of 0.60 g/cm^3. Similar phenomena are observed also in the case of a very powerful intermediate detonator. Thus, with the use as such a detonator of a pressed tetryl charge 20 g in weight, occurred full detonation of a charge made from dinitroaniline with a density of 0.71-0.72 g/cm^3 and diameter of 70 mm; an analogous charge with a density of 0.56 g/cm^3 in these conditions of initiation failed. For picramic acid the same results were received in pipes 40 mm in diameter at a charge density of 0.8 and 0.5 g/cm^3, correspondingly.

Discussion of Results

Proceeding from general presentations about the conditions of stability of detonation, developed by Yu. B. Khariton [3], the results obtained can be explained in the following manner.

The investigated dinitro compounds are systems with a low explosive ability and critical diameter of detonation for charges from them without a shell is great. In a durable and massive shell (metallic pipe), delaying the dispersion of the substance, detonation of such compounds becomes possible in a charge of small diameter. In the above described experiments, the explosion was initiated in a charge of small density and large diameter by such a method that in the first moment, the reaction appeared only in a section of the charge limited in diameter (for example, percussion cap-detonator or according to the diagram in Fig. 1). The substance, surrounding the focus of initiation, the reaction ability of which under the conditions of explosion is small, can behave as an inert shell. The small density of the substance makes it inertial resistance insignificant. A shell made of a substance of small density is easily packed. As a result of this packing, fast dispersion of the unreacted substance and products of incomplete reaction from the focus of initiation occurs, which leads to attenuation of the explosion in this focus. If the layer of packed substance between boundaries of the focus of initiation and the metallic shell is small, as this takes place in a conical charge at initiation from a smaller base of the cone, then dispersion of the substance due to packing is limited and cannot lead to attenuation of detonation.

It is clear that with identical dimensions of the focus of initiation, the dispersion of the explosive as a result of packing of the surrounding layers will be smaller, the greater their density. Precisely therefore there is observed, at definite conditions of initiation, detonation of charges of great density and their failure at lower density.

In a case, when the initiator creates a focus of initiation of sufficiently large dimension -- stable detonation occurs also in a charge in a pipe of large diameter. If, however, we use an even more powerful initiator (pressed charge of powerful explosive), then in charges of small density, the compression leading to packing of the substance, is spread faster than the explosive transformation. Before the front of the reaction, occurring in a definite layer of the dinitro compound is a consolidated substance, the receptivity of which to detonation is small. This phenomenon is analogous to that described by A. F. Belyayev [1] concerning attenuation of detonation of charges of ammonium nitrate and mixtures on its base at extremely strong initiation.

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Tape No. MT-63-254

Chapter 4 Article 43

Pages 561 - 579

G. G. Rempel'

43. Determination of Speeds of Shock Waves Necessary to Trigger Detonation of Explosives

The investigation of phenomena occurring during triggering of detonation presents not only theoretical but also practical interest. These investigations have special value for operations in mines, made dangerous by gas and dust.

Elements of the detonation chain should be selected so as to assure stable detonation of the entire charge with a speed "normal" for it. Of course, this requirement can be carried out only for charges capable of stable detonation.

Processes proceeding during the triggering of detonation are more complicated than phenomena, appearing during the propagation of the shaped detonation wave. However, triggering of detonation should in a significant measure be regulated by the same circumstances that regulate its stability. Consequently, a prerequisite for the study of process of triggering of explosion was the study of the phenomena determining stability of detonation.

Only after the main regularities determining stability of detonation and the dependence of its rate on charge diameter, dimension of particles and other factors were established as a result of the work of Yu. B. Khariton [5], A. F. Belyayev [3], A. Ya. Apin [1], V. K. Bobolev [4], et al., did fruitful study of the process of triggering of detonation become possible. The majority of the earlier works devoted to this question had the character of empirical selection of the necessary dimensions of detonators(strikers) or permissable thickness of layers between detonator and charge in one or another particular case, without physical interpretation of the data obtained.

In the opinion of the majority of investigators, the appearance of detonation is connected with the formation in the charge of a shock wave. If this wave possesses sufficient intensity, then behind its front a violent chemical reaction begins. Detonation appears. It is obvious that for its triggering, the shock wave must have parameters (in the first place speed) that are of no less than the critical magnitudes necessary for the development of the reaction behind the wave front. One could expect that these critical magnitudes should depend not only on such characteristics of the charge as its chemical composition and density, but also on conditions of the scattering of products of explosion, i.e., on those conditions that determine possibility of stable detonation.

It is obvious that to ascertain the regularities determining triggering of detonation it is in the first place necessary to know the magnitude of the velocity of the initiating shock wave required for the appearance of detonation, and also the dependence of this speed on the characteristics of the charge.

The only data on the necessary speeds of initiating shock waves were obtained by B. I. Shekhter [2], who established that in charges of pressed trotyl and flegmatized hexogen 23 mm in diameter (i.e., with diameters approximately 10 times greater than the critical for the given explosive) detonation appears in that case when the shock wave has a speed of 2400--3000 m/sec. Depth and area of the wave front in B. I. Shekhter's experiments remained constant.

Shock waves in the initiating charge were created by this investigator with the help of waves propagated by inert layers (water, steel, etc.), which removed the possibility of direct influence of the products of the explosion of the active charge (detonator) on the passive charge.

However, after the experiments of B. I. Shekhter it remained, as before, unknown just how the minimum speeds of shock waves necessary for triggering detonation will vary in relation to the diameter of the passive charge, the size of its particles, and other factors.

The question of what the speed of the initiating wave should be under the conditions most frequently met in practice during direct contact of the active and passive charges was also left vague.

To clarify these questions the work whose results are outlined in the present article was carried out.

The direct determination of the speed of shock waves appearing at the beginning passive charge presents significant difficulties. However, the speed of the shock wave can be judged by the speed of detonation in the case when detonation immediately appears in the passive charge and recording of its true rate is possible.

With optical methods of registering the detonation rate of an opaque charge, the latter condition is fulfilled only if the wave from the very beginning is spread with a constant radius of curvature. If there is an increase in this radius, the exit of the wave on the surface at the beginning of the charge occurs with a higher speed than the movement along the axis, as a result of which an oversized value of speed is recorded on the initial section.

The speed of the shock wave appearing at the beginning of the initial charge can also be judged by the rate of detonation of the active charge or by the speed of the shock wave propagated by the inert layer, through which detonation is transmitted.

Although the speed of the shock wave appearing at the beginning of the charge is not equal to the detonation rate of the active charge or the speed of the wave in the inert layer, it should be clearly connected with them. The higher the detonation rate of the active charge, the greater will be (other conditions being equal) the speed of the shock wave appearing in the initiated (passive) charge.

In the particular case when the density and compressibility of the substance of the active charge are equal to those of the substance of the passive charge, the speed of the shock wave at the beginning of the passive charge will be equal to the detonation rate of the active charge (in the presence of contact of the active and passive charges).

Thus, the shock wave speed necessary for triggering detonation in the passive charge can be judged by the rate of detonation appearing at the beginning charge, if there is confidence in the absence of distortions during its recording, and by the detonation rate of the active charge or by the speed of the shock wave in the inert medium adjoining the charge.

The ability of a shock wave to excite an intense chemical reaction behind its front or, in other words, the capability of a shock wave created in a charge to pass to detonation depends not only on its speed, but also on its depth more accurately on the character of the change in pressure behind the wave front, and on the area and form of the wave front.

The most favorable conditions for triggering detonation are created during the action of a plane wave or of a wave having small curvature and great depth. Small curvature of the front of the initiating shock wave created at the beginning passive charge also removes the possibility of significant distortions in recording the detonation rate on the initial section of the charge.

Therefore in conducting the experiments it was desirable to produce initiation by waves with the largest possible depth of the pressure zone and a large radius of curvature of the wave front. This could be achieved by using as detonators charges of great height enclosed in a strong massive shell or having large diameter.

As passive charges it was decided to use at first charges of cast and pressed trotyl. In the future work with charges of the practically utilized ammonite is anticipated.

Experimental Part

Three groups of experiments were set up.

1. Charges of cast trotyl were initiated by explosions of charges of a pressed mixture of trotyl with talc.

2. Such charges were initiated by explosions of charges of filled trotyl or a mixture of it with alabaster.

3. Detonation in charges of pressed trotyl was triggered excited by a shock wave propagated through water.

Triggering Detonation of Charges of Cast Trotyl by Explosions of Pressed Charges of a Mixture of Trotyl With Talc

As passive charges we used charges of cast small-crystal trotyl, prepared by casting in split metallic forms of various diameters.

As active charge we used pressed charges 32 mm in diameter, made from a mixture of trotyl with talc; they were placed in a steel pipe with an internal diameter of 32 mm and wall thickness of 4 mm. Ten charges were placed in the pipe. Due to the great length of the charge and the presence of the massive shell, the wave appearing on the face of such a charge should have large depth and a great radius of curvature.

Before preparation of the mixture the trotyl and talc were sifted through a No. 24 sieve.

In all experiments we determined the detonation rate of the active charge and established either the appearance of detonation or refusal in the passive charge. In part of experiments the detonation rate was measured with the help of a photoregister with mirror scanning (SFR-2). In this case we also determined the detonation rate at the beginning of the passive charge. In remaining experiments the detonation rate of the active charge was measured by the method of Dotrish.

In the experiments with the photoregister the active and passive charges were fastened to a wooden rod or brass plate so that their faces touched and their axes coincided.

In the wall of the pipe in which the active charge was enclosed there was a slot turned toward the photoregister. The completeness of detonation of the initiated (passive) charge was judged by the photographic print and the imprint on the brass plate.

In those cases when the detonation rate of the active charge was determined by the Dotrish method, the active and passive charges were packed on thin steel sheet. The completeness of detonation of the passive charge was judged by the imprint on the sheet.

Variation of the detonation rate of the active charge was attained by changing the density and contents of components in the charges made of a mixture of trotyl with talc.

The diagram of the experiments with the photoregister is shown in Fig. 1 and samples of the photographs of the detonation of active and passive charges in Figs. 2 and 3.

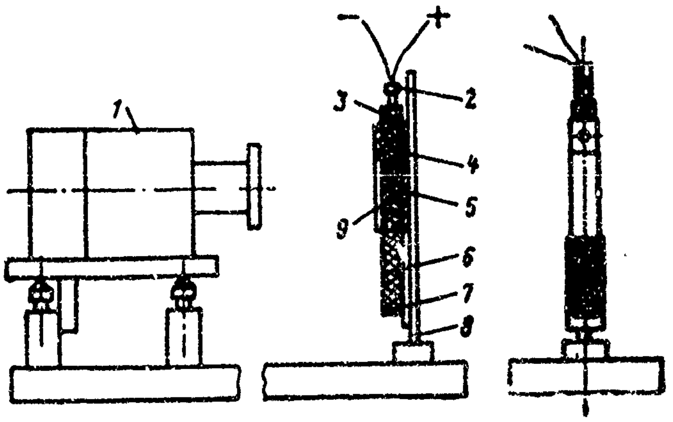

Fig. 1. Diagram of initiation of a charge of cast trotyl by a charge of a pressed mixture of trotyl and talc, with measurement of detonation rate by a photoregister. 1 — photoregister; 2 — percussion cap; 3 — intermediate detonator; 4 — active charge (mixture of trotyl with talc); 5 — steel pipe; 6 — passive charge (cast trotyl); 7 — brass plate; 8 — wooden rod; 9 — slot in pipe.

In Fig. 2 is shown a photograph obtained during an experiment experience on initiation of a charge 22 mm in diameter of cast small-crystal trotyl by the explosion of a charge of a pressed mixture of 70% trotyl and 30% talc, 32 mm in diameter, without a shell. The detonation rate of the mixture was 5400 m/sec.

In the cast trotyl detonation appeared and was spread to the end of the charge als with a speed of 5400 m/sec.

Fig. 2. Photograph obtained during experiments on initiation of charge 22 mm in diameter of cast trotyl. 1 — end of active charge; 2 — Trace of detonation of passive charge.

Fig. 3. Photograph obtained during an experiment on the initiation of a charge 32 mm in diameter of cast trotyl. 1 — trace detonation of active charge, visible in slot; 2 — boundary of active and passive charges; 3 — section of acceleration of detonation of passive charge; 4 — end of section of acceleration; 5 — section of stable detonation of passive charge.

In Fig. 3 is shown a photograph obtained during an experiment on the initiation of charge 32 mm in diameter of cast small-crystal trotyl by the explosion of a charge of pressed mixture 45% trotyl and 55% talc 32 mm in diameter in a steel pipe with a wall thickness of 4 mm. In the wall in the lower part of the pipe there was a slot 4 mm in width. In the given experiment the detonation rate of the active charge at the moment of approach to the cast trotyl was 3300 m/sec (weak glow). The detonation rate appearing in the cast trotyl was in the beginning approximately equal to that of the active charge. However, at a distance of 30--35 mm from the beginning of the passive charge its detonation rate increased to 6500 m/sec, after which it was propagated with this speed.

In the majority experiments in which explosions of passive charge were observed; detonation of cast trotyl appeared without delay and its rate in the beginning was equal to the detonation rate of the active charge of a mixture of trotyl with talc, and then increased or remained constant.

However in certain experiments there occurred delay or deceleration of detonation during passage of the wave from the pressed mixture to the cast trotyl. Unfortunately, in such experiments we did not succeed in obtaining a clear picture of the phenomena occurring at the place of contact of the passive and active charges. The dependence of this phenomenon on the detonation rate of the active charge also was not detected. For example, delay was observed with a detonation rate of the active charge of 3500 m/sec, then at a detonation rate of the active charge of 3300 m/sec a passive charge of cast trotyl started to detonate without delay (Fig. 3).

From analysis of the photograph obtained the following conclusions can be drawn:

During initiation of cast trotyl by explosions of charges of a pressed trotyl--talc mixture in most cases there appears in the passive charge wave detonation whose speed is equal to the detonation rate of the active charge. This speed is

Table 1

Triggering of detonation of cast trotyl by explosions of pressed charges of a mixture of trotyl with talc

3) Диаметр пассивного заряда из литого тротила в мм	1) Определено по Лотришу					2) Определено на фоторегистре		
	4) Скорости, при которых возникает детонация пассивного заряда в м/сек			5) Скорости, при которых детонация пассивного заряда не возникает в м/сек		4) Скорости, при которых возникает детонация пассивного заряда в м/сек		5) Скорости, при которых детонация пассивного заряда не возникает в м/сек
50	3400	3350	3000	6) Отказов не было				
40	5650	4700	4200					
	3750	3600	3050	7) То же				
32	5000	4200	3950	2000	2050	3500	3400	2300
	3750	3700	3650	2400	-	3400	3300	3100
	3800	3600	3600	—	—	3000	2600	—
	3650	3550	3500	—	—	—	—	—
	3400	3300	3300	—	—	—	—	—
	3250	3100	[illegible]	-	—	-	-	—
	2950	2700	2700	—	-	—	—	—
	2600	—	—	—	—	—	—	—
28	5400	4750	4600	2000	2450	3500	3200	3200
	4200	3900	3300	3000	3300	3300	—	2800
	—	—	—	3300	—	—	—	—
22	6600	5100	4200	3000	3150	—	—	2800
	—	—	—	3400	3600	5500	5400	3400
	—	—	—	3750	3200	3500	—	3600
	—	—	—	4100	—	—	—	—
21	—	—	—	—	—	4400	—	8700

1) Determined according to Dotrish; 2) Determined on photoregister; 3) Diameter of passive charge of cast trotyl, in mm; 4) Speed with which detonation of passive charge appears, in m/sec; 5) Speed with which detonation of passive charge does not appear, in m/sec; 6) There were no refusals; 7) The same.

quickly increased. At a distance of 30 — 60 mm from the beginning of the passive charge the detonation rate will attain its own normal value (for the given diameter of a charge of cast trotyl). On the basis of this it is possible to consider that the speed of the shock wave appearing in the cast trotyl is approximately equal to the speed of the detonation wave in the mixture of trotyl with talc.

During triggering of detonation in cast trotyl charges of small diameters, close to the critical, the charges can detonate at a constant rate, given to them by the active charge (in any case with a length of charge of up to 200 mm).

The distortion usually appearing at the beginning of the passive charge during measurement of detonation rate on a photoregister was in these experiments eliminated, or in any case, reduced to a minimum.

In Table 1 are given the results of experiments in which we determined the minimum detonation rate of an active charge of a trotyl — talc mixture necessary to trigger detonation in cast small-crystal trotyl.

Triggering Detonation of Cast Trotyl Charges by Explosions of Small Density Charges of Pulverized Trotyl or its Mixture With Alabaster

The active charges were paper cylinders 0.6 m in length, filled with pulverised trotyl sifted through a No. 24 sieve or mixtures of this trotyl with alabster.

Passive charges — trotyl, cast.

Active and passive charges were packed on steel sheets so that their faces touched and their axes coincided. The detonation rate of the initiating charge was measured according to Dotrish. The completeness of detonation of the initiated charge was judged by the imprint on the slab.

Characteristics of the initiated and initiating charges and the results of the experiments are given in Table 2.

Table 2

Triggering the detonation of cast trotyl by explosions of low-density charges of pulverized trotyl or mixtures with alabaster

1) Пассивный заряд		2) Активный заряд					7) Результаты опыта
3) Вещество	4) Диаметр *мм*	3) Вещество		4) Диаметр *мм*	5) Плотность *г/см³*	6) Скорость детонации *м/сек*	
8) Тротил литой, отливка мелкокристаллическая	100	9) Тротил насыпной, измельченный		44	0,9	4600	10) Детонация
	80	11) То же		88	1,0	5000	.
	80	.		80	1,0	5000	.
	44	.		44	1,0	5000	.
	40	.		32	0,95	4600	.
	34	.		32	1,0	4800	.
	32	.		32	1,0	4700	.
	32	.		32	1,0	5000	.
	32	.		32	1,0	4600	.
	21	.		80	0,95	4600	.
	28	.		80	0,96	4700	.
	80	12) Смесь тротила с алебастром	80/20	80	1,0	4450	.
	80	11) То же	70/30	80	1,0	4100	.
	80	.	50/50	80	1,0	2450	.
	80	.	40/60	80	1,0	—	.
	60	.	60/40	60	1.1	3000	.
	52	.	50/50	80	1,1	2450	.
	40	.	50/50	80	1,1	2700	13) Затухание
	32	.	50/50	80	1,1	2700	10) .
	32	.	50/50	150	1,2	2850	Детонация

1) Passive charge; 2) Active charge; 3) Substance; 4) Diameter, mm; 5) Density, g/cm³; 6) Speed of detonation, m/sec; 7) Results of experiment; 8) Cast trotyl, small-crystal castings; 9) Filled trotyl, pulverized; 10) Detonation; 11) The same; 12) Mixture of trotyl with alabaster; 13) Attenuation.

Triggering of Detonation of Pressed Trotyl Charges by Shock Waves, Propagated in Water

Assembly of active and passive charges in these experiments was done according to the diagram shown in Fig. 4.

On the bottom of test-tube 2, made of acetyl cellulose and having an internal diameter of 23.5 mm, we set up 2 charges of flegmatized hexogen (density 1.58 —

1.60 g/cm^3), with diameters of 23 mm and a general height of 57 — 60 mm, serving in all experiments as active charge 3. Then the test-tube was filled with water until the height of its layer above the charges attained the needed magnitude.

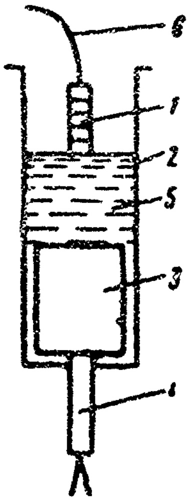

Fig. 4. Diagram of experiments on triggering detonation through a layer of water. 1 — passive charge; 2— test-tube; 3 — active charge; 4 — detonating cap; 5 — water; 6 — wire.

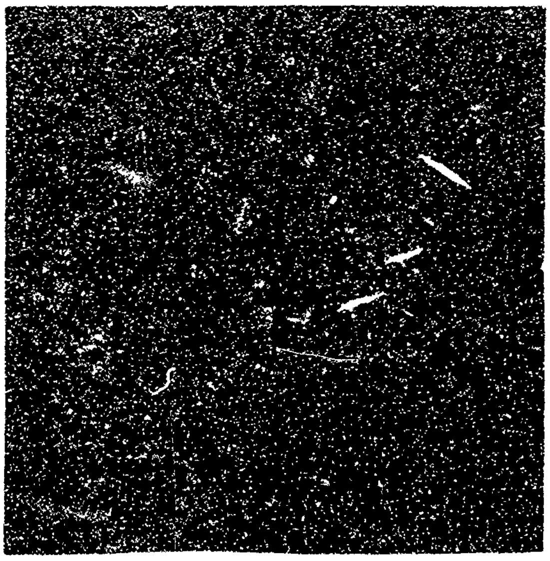

Fig. 5. Photograph obtained during transmission of detonation through a layer of water. 1 — trace of detonation of active charge; 2 — end of active charge; 3 — beginning of detonation of passive charge; 4 — trace of products of detonation of active charge, moving behind the ejected water; 5 — trace of detonation of passive charge.

During experiments with passive charges of pressed trotyl, sifted through a No. 52 sieve, with diameters of 3.85 to 23 mm, we lowered into the test-tube copper wire 6 with a column of charges attached to it, representing passive charge 1. The face of the lower charge was brought into contact with the surface of the water so that there was no air layer between the charge and the water and so that the immersion of the charge in the water did not exceed 0.5 mm. During experiments with passive charges 23 mm in diameter, a cartridge consisting of two charges was lowered on threads into the test-tube, which was attached to a brass plate.

The completeness of detonation of the passive charge was judged by the deformation of the copper wire or brass plate.

In some of the experiments the detonation rate was determined with the help of a photoregister.

In Fig. 5 is shown a photograph obtained during transmission of detonation from the active to the passive charge through a layer of water.

As the active charge in this experiment we used two charges of pressed flegmatised hexogen with a general height of 60 mm, and as the passive charge — a charge 8 mm in diameter of trotyl, pulverized and sifted through a No. 52 sieve, having a density of 1.59 g/cm^3. The thickness of the layer of water constituted 18 mm.

In Fig. 5 is seen the section of acceleration of detonation in the passive charge. The glow on the section of acceleration was weak. The average speed on the section of acceleration was 4500 — 5000 m/sec. The speed of the shock wave in water at a distance of 18 mm from a passive charge 23 mm in diameter was approximately equal to 3900 m/sec. Transition to the normal speed of detonation — 6700 m/sec — was accompanied a sharp growth in the intensity of glow.

In Fig. 5 is seen also the trace of products of detonation of the active charge, moving behind the ejected water. This trace approaches the passive charge later than detonation appears in the latter.

The results of experiments on the transmission of detonation through a layer of water are given in Table 3.

In Table 4 are shown the minimum speeds, required for a shock wave in water for triggering of detonation in charges of pressed pulverized trotyl of various diameters, and the calculated values of the speeds of shock waves appearing in pressed trotyl.

The approximate calculation of the latter was conducted under the assumption that the equation of state of pressed trotyl at large pressures has the form

$$P \approx p^k,$$

where p — density of the explosive and k = 8. Passive charges had a density of

1.58 g/cm^3.

Table 3

Triggering of Detonation of Pressed Trotyl Through a Layer of Water

1) Пассивный заряд		4) Толщина слоя воды между активным и пассивным зарядами в *мм*	5) Результаты опыта	6) Толщина слоя воды, при которой обеспечивается детонация зарядов данного диаметра в *мм*
2) Диаметр *мм*	3) Плотность *г/см*^{3}			
23	1,58	30	Отказ 7)	
23	1,57	30	•	
23	1,57	28	•	
23	1,57	25	Детонация 8)	25
23	1,57	25	•	
10	1,58	28	Отказ 7)	
10	1,58	25	Детонация 8)	25
8	1,59	20	Отказ 7)	
8	1,59	18	Детонация 8)	18
8	1,59	18	•	
5,85	1,58—1,61	28	Отказ 7)	
5,85	1,58—1,61	25	•	
5,85	1,58—1,61	20	Детонация 8)	
5,85	1,58—1,61	18	•	
5,85	1,58—1,61	15	•	
5,85	1,56—1,58	20	Отказ 7)	
5,85	1,56—1,58	20	•	
5,85	1,56—1,58	18	Детонация 8)	18
5,85	1,51—1,55	25	Отказ 7)	
3,85	1,56—1,61	15	•	
3,85	1,56—1,61	15	•	
3,85	1,5 —1,56	15	•	
3,85	1,56—1,61	12	Детонация 8)	12
3,85	1,56—1,61	12	•	
3,85	1,5 —1,56	12	•	

1) Passive charge; 2) Diameter, mm; 3) Density, g/cm^3; 4) Thickness of layer of water between active and passive charges, in mm; 5) Results of experiment; 6) Thickness of layer of water with which detonation of a charge of the given diameter, in mm is assured; 7) Refusal; 8) Detonation.

Table 4

Minimum speeds of shock wave in water for triggering detonation of pressed trotyl charges of various diameters

1) Диаметр пассивного заряда *мм*	2) Прослойка воды, через которую передается детонация, *мм*	3) Скорость ударной волны в воде *м/сек*	4) Скорость ударной волны в прессованном тротиле *м/сек*
10	25	3160	2700
5,85	18	3860	3500
5,85	12	4760	4500

1) Diameter of passive charge, mm; 2) Layer of water through which detonation is transmitted, mm; 3) Speed of shock wave in water, m/sec; 4) Speed of shock wave in pressed trotyl, m/sec.

Discussion of Results

The minimum speeds of shock waves necessary for the appearance of detonation in charges of cast and pressed trotyl of various diameters are shown in Table 5.

In Table 5 are presented in a form very convenient for analysis the results of tests of the dependence of minimum speed of the initiating shock wave on relative diameter, i.e., on the magnitude of the ratio d/d_{crit}, where d is the actual diameter of charge and d_{crit} is the critical diameter. Use of such dependence was proposed by A. F. Belyayev [3].

The critical diameter for small-crystal cast trotyl was taken to be equal to 20 mm and that for pressed trotyl, 3.5 mm.

The dependence of the minimum necessary speeds of the initiating wave (D_{init}) on the absolute and relative charge diameters is depicted in Figs. 6 and 7. On these figures is shown the dependence of the speed of established detonation D_{ch} on the charge diameter for small-crystal cast trotyl (according to literature data).

The speed of the initiating shock wave that must be created at the beginning of a charge for detonation to be triggered in it depends on its diameter. The less the diameter of charge, the bigger is the required wave speed. With charge diameters significantly larger than the critical, the speed of a shock wave assuring triggering of detonation approaches the speed of sound in the substance.

Values of the latter were determined in a separate work. In cast trotyl with a density of 1.58 g/cm^3 the speed of sound is 2100 m/sec and in pressed trotyl with the same density — 1900 m/sec. At diameters, close to the critical, the minimum speed of the initiating shock wave approaches the so-called critical speed of detonation, i.e., the speed at which that a charge of critical diameter usually detonates. For cast and pressed trotyl these speeds are approximately equal to 4200 — 4500 m/sec.

One should note that with the methodology used in this work, where the initiating waves had large depth and small curvature, especially favorable conditions for triggering of detonation were created. At the smaller depths of initiating wave that usually occur in practice, a somewhat higher speed of the initiating shock wave will be required to trigger detonation.

Table 5

Dependence of minimum speeds of shock waves /required/ to trigger detonation of cast and pressed trotyl charges on the relative diameter of the charges

1) Характеристика активных зарядов	2) Характеристика пассивных зарядов	Диаметр пассивного заряда 3) *мм*	11) $d/d_{кр}$	Минимальная скорость инициирующей 4) волны *м/сек*
5) Шашки диаметром 32 *мм* из прессованной смеси тротила с тальком в стальной трубе	8) Мелкокристаллический литой тротил (ρ=1,58÷1,59 *г/см*^{3})	22	1,10	4200
		23	1,14	3800
		26	1,30	3300
		32	1,60	2600
6) Насыпной измельченный тротил или его смеси с алебастром	9) Литой мелкокристаллический тротил	32	1,60	2650—2700
		52	2,40	2450
7) Шашки диаметром 22 *мм* из флегматизированного гексогена. Возбуждение детонации производилось ударной волной, распространявшейся в воде	10) Прессованный тротил, просеянный перед прессованием через сито № 52 (ρ=1,5÷1,61 *г/см*^{3})	3,85	1,10	4500
		5,85	1,65	3600
		10,00	2,85	2700

1) Characteristic of active charge; 2) Characteristic of passive charge; 3) Diameter of passive charge, mm; 4) Minimum speed of initiating wave, m/sec; 5) Charge 32 mm in diameter of a pressed mixture of trotyl with talc in a steel pipe; 6) Filled pulverized trotyl or its mixture with alabaster; 7) Charge 23 mm in diameter of flegmatized hexogen. Triggering of detonation was produced by a shock wave propagated in water; 8) Small-crystal cast trotyl (ρ = 1.58 to 1.59 g/cm^3); 9) Cast small-crystal trotyl; 10) Pressed trotyl, sifted before pressing through a No. 52 sieve (ρ = 1.5 to 1.61 g/cm^3); 11) d/d_{crit} .

As we have seen, with a decrease in the charge diameter the minimum speed of the initiating wave necessary to trigger detonation in it increases. This phenomenon indicates that with a small wave speed there is an increase in the relative losses from the zone of reaction created at the beginning of the charge. An increase in losses can take place only in the case when the length of the zone of this reaction grows simultaneously with deceleration. If the increase of reaction time with

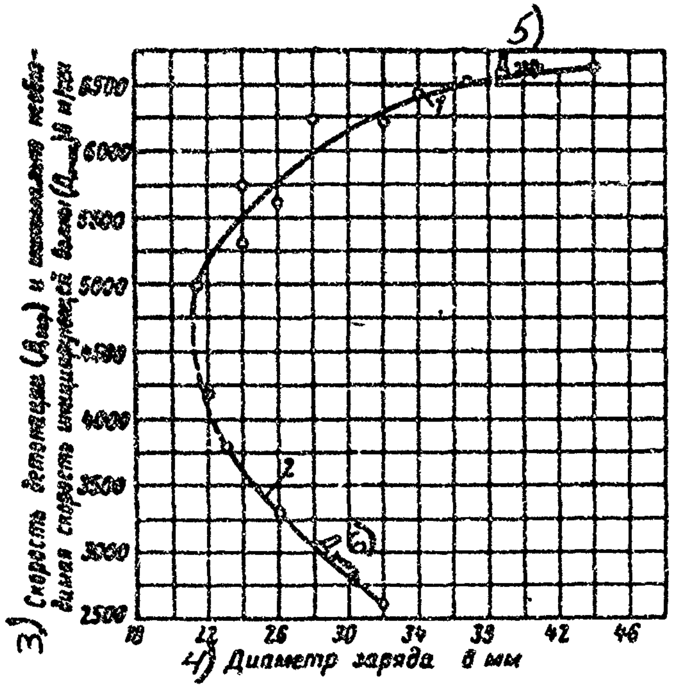

Fig. 6. Dependence of detonation rate and minimum necessary speed of initiating wave on diameter of initiated charge of cast trotyl. 1) speed of detonation; 2) minimum speed of initiating wave necessary for appearance of detonation; 3) Detonation rate (D_{ch}) and minimum necessary speed of initiating wave (D_{init}) in m/sec; 4) Diameter of charge in mm; 5) D_{ch}; 6) D_{init}.

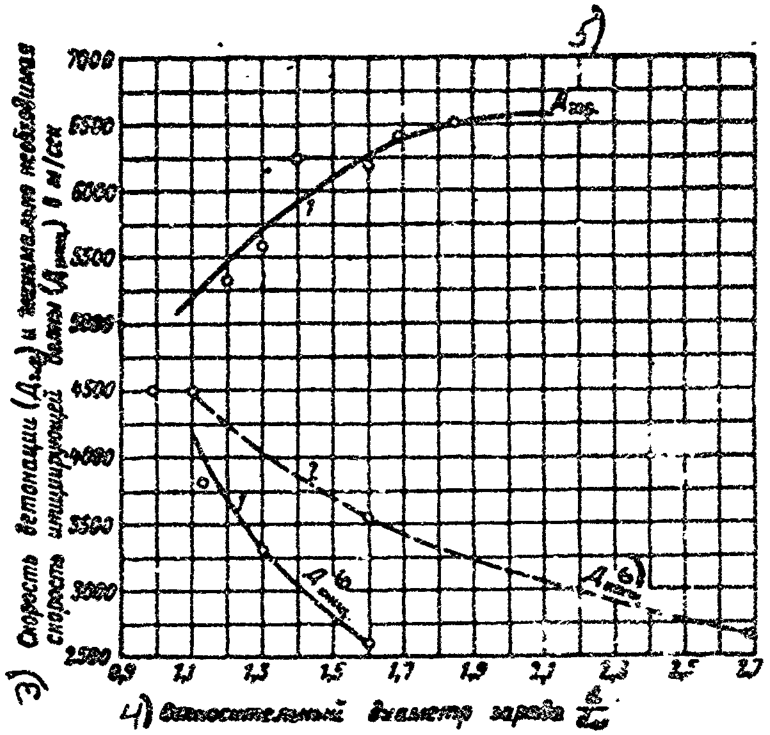

Fig. 7. Dependence of detonation rate and minimum necessary speed of initiating wave on the ratio d/d_{crit} for charges of cast and pressed trotyl. 1) Small-crystal cast trotyl; 2) Pressed trotyl; 3) Detonation rate (D_{ch}) and minimum necessary speed of initiating wave (D_{init}) in m/sec; 4) Relative diameter of charge d/d_{crit}; 5) D_{ch}; 6) D_{init}.

lessening of the wave and the temperature on its front is obvious, requires no checks, growth of length of the reaction zone with deceleration of initiating wave is itself not obligatory.

In reality the length of the reaction zone $l \sim D\tau$,

where D is the detonation rate in m/sec, and

τ is the reaction time in sec.

With deceleration of the initiating wave, l can remain constant, since with decrease in D there is an increase in τ, and their product cannot change.

The data obtained show that in reality (in any case for trotyl charges) the length of the reaction zone increases with deceleration of the wave and this can happen only when τ increases faster than D decreases.

The rate of detonation appearing at the beginning of the passive charge depends on the detonation rate of the active charge or on the speed of the shock wave in the medium through which detonation is transmitted.

As can be seen from the graphs of Figs. 6 and 7, the curves of the dependence of the speed of the initiating wave and of detonation rate on charge diameter cross at $d = d_{crit}$.

The speed corresponding to the point of intersection is, obviously, the critical detonation rate. One should note that up to now the determination of the critical detonation rate met significant difficulties, since near the critical diameter the detonation rate drops very fast and a small impairment of quality of charge is sufficient for propagation of detonation to become impossible.

The determination of critical speeds by the point of intersection of curves $D_{init} = f(d)$ and $D_{ch} = f(d)$ allows to refine their value for various explosives.

As can be seen from the graph of Fig. 6, $D_{crit} = 4500 - 4600$ m/sec for cast trotyl. In accordance with the data of A. Ya. Apin [1] and V. K. Bobolev [4], the critical detonation rate does not depend on the grain size of the explosive.

Thus, for appearance of detonation in charges whose diameter of that is equal to the critical, it is necessary to create a shock wave whose speed should be no less than the normal detonation rate of such charges.

With an increase in charge diameter the required speed of the initiating shock wave is decreased, asymptotically approaching the speed of sound in the given explosive.

As can be seen from the curves in Fig. 7, the speed of shock waves which must be created to trigger charges of cast and pressed trotyl are near enough to each other at identical d/d_{crit}.

A certain increase in the speed of shock wave, required for appearance of detonation of charges of pressed trotyl, is probably explained by the fact that the triggering of detonation during the initiation of cast trotyl was somewhat relieved by the thermal influence of products of the explosion of the initiating charge. During excitation of pressed trotyl detonation was transmitted through a layer of water and the thermal influence therefore was excluded.

General Conclusion

1. The speed of the initiating shock wave that must be created in a charge for detonation to appear depends on charge diameter. For charges of critical diameter $D_{init} = D_{crit}$. With an increase in diameter, D_{init} is decreased asymptotically, approaching the speed of sound in the substance.

2. With deceleration of the detonation wave in trotyl charges the length of zone of chemical reaction behind the wave front is increased.

3. Accurate value of the critical rate detonation (speed at which that a charge with a diameter equal to the critical detonates) can be determined by the point of intersection of curves of $D_{init} = f(d)$ and $D_{ch} = f(d)$.

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