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SOLID PROPELLANT COMBUSTION

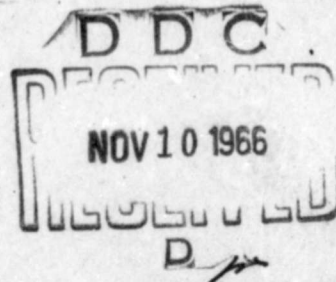
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Analytical Survey

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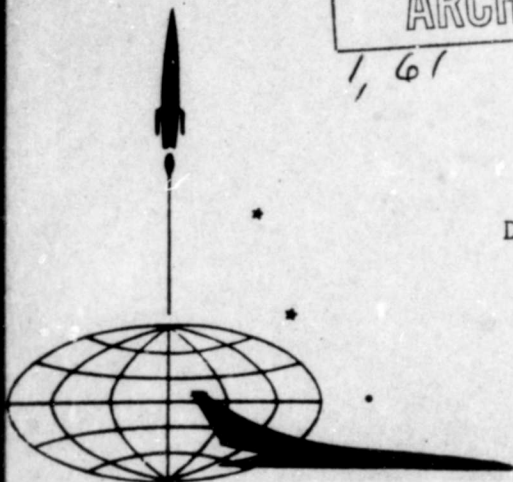
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Abstract

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This analytical survey is based on Soviet open sources published 1962-1966. It consists of two parts: Part I contains a general discussion of selected articles on solid propellant combustion and Part II comprises the abstracts of these articles. The information in Part I is divided into 8 sections: 1. The effect of pressure; 2. Particle size, porosity, and density; 3. The effect of temperature; 4. Condensed phase reactions; 5. Ignition characteristics; 6. Additives and catalytic effects; 7. Theoretical stability criteria; 8. Miscellaneous. The material reviewed indicates that Soviet investigators are placing particular emphasis on the following three areas: the relationships between the pressure and the burning velocity; the effect of porosity, particle size, and density on burning velocity and instability; and condensed-phase reactions. These three subjects are discussed somewhat further by the analyst in the Introduction which includes the analyst's evaluation of Soviet combustion research. Part II includes 73 abstracts. There is no bibliography.

8 August 1966

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SOLID PROPELLANT COMBUSTION

Analytical Survey

ATD Work Assignment No. 68

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FOREWORD

This analytical survey, dealing with solid propellant combustion, is based on Soviet open literature available at the Aerospace Technology Division and the Library of Congress. The survey covers the period from January 1962 through May 1966. Approximately half of the abstracts presented in this survey have been previously published in the ATD Press, and some of these topics have been previously discussed in other ATD publications.

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INTRODUCTION

The survey consists of two parts: Part I contains a general discussion of selected articles on solid propellant combustion, and Part II, the abstracts of these articles. The material reviewed indicates that Soviet investigators are placing particular emphasis on the following three areas: the relationships between the pressure and the burning velocity; the effect of porosity, particle size, and density on burning velocity and instability; and condensed-phase reactions. These three subjects are important for elucidating combustion instability phenomena and general combustion characteristics. The pressure sensitivity of the burning velocity may be considered to be an important characteristic for assessing instability. The particle size affects the pressure sensitivity of the burning velocity and is, therefore, an important parameter of stability. The porosity is important for gas penetration into the pores and pore wall ignition which, under given conditions, precedes instability and a deflagration to detonation transition. Condensed-phase reactions play an important role, since by shifting the controlling reaction from the condensed into the gas phase or from the gas to the condensed phase, stability characteristics are markedly affected.

It is evident from the current literature that Soviet researchers are making great progress and are showing an original approach to the study of combustion mechanisms and instability phenomena.

SOLID PROPELLANT COMBUSTION

PART I. GENERAL DISCUSSION

1. THE EFFECT OF PRESSURE

The effect of pressure on the burning velocity and other combustion characteristics is an important factor in stability analysis, since a change in pressure caused either by thrust control or nonuniformities in the combustion process may induce transient regimes leading to instability or to extinction. Consequently, Soviet researchers have made extensive investigations of this phenomenon.

An interesting analysis (50) was recently published by B. V. Novozhilov, who considered a burning solid propellant to be an oscillating system and derived criteria for resonance and damping in response to harmonic pressure fluctuations. The same author in a previous study (53) derived expressions for determining the deviation of pressure from the steady-state value during harmonic pressure fluctuations. He considers this problem to be important in analyzing the generation of acoustic oscillations. The effect of rectangular and triangular pressure pulses on the combustion characteristics was also analyzed (22), and the conditions were established under which pressure pulses may lead to extinction. An analysis (20) of the pressure dependence of the burning velocity based on the relaxation theory is presented, and the range of pressure exponential values in the burning velocity vs pressure relationship were calculated. Analytical expressions for calculating the nonsteady-state burning velocity were obtained on the basis of a theoretical model (24). Another theoretical study on the effect of pressure on the burning velocity was presented in (72).

An interesting analysis of the anomalous dependence of the pressure on the burning velocity of ammonium perchlorate was made on the basis of a theoretical model (41). This model considered the interaction between the gas-phase and the condensed-phase reaction zones. It was found that either zone can be rate controlling depending on the pressure (41).

Several experimental studies deal with the combustion characteristics of ammonium perchlorate and its mixtures with various fuels. A study which seems to be important for evaluating performance characteristics of composite propellants was published by Belyayev (14), who studied the burning velocity vs pressure relationship of mixtures of perchlorate with finely ground trotyl, asphalt, polystyrene, and paraformaldehyde. At subatmospheric pressures, all relationships were linear. It was concluded that depending on the pressure, four different combustion regimes exist. At higher pressure (100—1500 atm), the burning velocity vs pressure relationship is nonlinear and multiflame fronts may occur. The latter are characterized by flame centers on the

burning surface which are caused by the propagation of flame along the fuel-oxidizer boundaries. Nonlinear burning velocity vs pressure relationships and multiflame fronts appear to be indicative of potential instability. The results of this study also point to the importance of the structure of the burning surface.

The thermal decomposition of ammonium perchlorate at 1 to 100 atm and 230—260°C was studied (65). Temperature fluctuations in the combustion of ammonium perchlorate at 40—350 atm were measured and used for characterizing stable and unstable combustion regimes (16). Combustion of ammonium perchlorate at high pressures up to 1000 atm was also studied (21). The structure of the grain surface of stoichiometric mixtures of perchlorates with graphite, naphthalene, starch, etc. was studied at up to 100 atm (54). The burning velocities of smokeless powder and PETN with various additives was determined (13) as a function of pressure at 10—110 atm. It was found that the presence of charcoal markedly increases the burning velocity; this is attributed to the generation of dispersed incandescent carbon particles (13). A method for determining the nonsteady-state burning velocities by measuring the pressure changes during combustion in a bomb is described (30). A method was described (10) for calculating the pressure increase at the burning surface of a solid propellant.

To summarize, it may be said that the effect of pressure or pressure changes on the burning velocity is considered by Soviet authors to be of great fundamental and practical interest which is reflected by the comparatively large number of studies devoted to this subject. Particular emphasis was placed on anomalies in pressure vs burning velocity relationships (e.g., 20, 41). Certain pressure vs burning velocity relationships appear to be indicative of instability, but the fundamental causes of instability seem to be connected with more complex physicochemical mechanisms which are controlled by the grain structure, porosity, reaction kinetics, etc., which are covered elsewhere in this report.

2. PARTICLE SIZE, POROSITY, AND DENSITY

The particle size of the fuel and the oxidizer is an important factor which controls the burning velocity and may also affect combustion stability. The problem of whether large, small, or mixed particles give more stable combustion has been the subject of several investigations. N. N. Bakhman (6) found

that by using small metal particles of W or Al (which do not gasify) in $W + KClO_4$ and $Al + Fe_2O_3$ mixtures, the burning velocity could be increased by a factor of up to 50. However, when the particle size in a propellant in which both components are gasified is increased, the velocity can be increased by a factor of only 2—4. This indicates that the particle size has the most significant effect in propellants where the condensed-phase reaction controls the combustion process. The burning velocity of mixtures with large particles was found less pressure dependent than that of mixtures with small particles. This finding may be important since the pressure dependence of the burning velocity may be indicative of instability. With a $KClO_4$ -graphite mixture, a converse relationship between the pressure dependence of the burning velocity and particle size has been detected. A comprehensive analysis of these relationships with allowance for the diffusion of the oxidizer through the molten reaction products was made by the same author (9). Bakhman also recently studied NH_4ClO_4 -plexiglass mixtures and found that certain peculiarities in the effect of the fuel and oxidizer particle size on the burning velocity can be explained by their decomposition rate and, consequently, by the composition of the gasified mixture in controlling the combustion zone (11). Small particle size NH_4ClO_4 burned slower than mixtures with larger particles. Bakhman investigated this problem (68) and found that in the case of an oxidizer with mixed particle size, the pressure dependence of the burning velocity depends on the fuel-oxidizer ratio. Depending on a parameter expressed in terms of burning velocities for large, small, and mixed particles, the burning velocity with mixed oxidizer particles can be either more or less pressure dependent than an oxidizer with either large or small particles. The use of a broader particle size range has been found in previous investigations to reduce the dependence of pressure on the burning velocity. N. N. Bakhman also presented another noteworthy paper (8), in which he theoretically derived formulas for calculating the dependence of the burning velocity on the particle size allowing for inhomogeneities in the mixture. N. N. Bakhman also investigated the effect of the size of Al, Ti, W, and Zr particles on the burning velocity of $KClO_4$ -asphalt mixtures (7). He found that the burning velocity has a minimum at a given particle size.

The porosity of a propellant has been considered in several Soviet studies to be an important factor in assessing stability characteristics since the penetration of combustion products into the pores or a nonuniform gas flow from the pores may lead to a deflagration to detonation transition or to instability. An investigation (17) of the effect of particle size and porosity of hexogen indicated that in the perturbed regime when the particle size increased, the duration of luminosity pulsations also increased. When the particles were coated with paraffin wax, the onset of the perturbed regime and the deflagration to deton-

ation transition were retarded. This is attributed to the fact that the wax acts as a thermal barrier and lessens the effect of the hot gases penetrating into the pores.

A comprehensive theoretical analysis (40) was made of the conditions under which the pore walls of a solid propellant can ignite during combustion. The gases can have a thermal effect such as ignition, pyrolysis, or heating of the propellant or a mechanical effect such as break-up of the propellant. Two different modes of penetration of gases into the pores exist: forced penetration caused by an increase in the outer pressure far from the propellant surface. In this case, the pore walls are ignited by hot gases, or by adiabatic or shock compression of gas inclusions. Spontaneous penetration of gases is caused by nonuniformities of the burning surface, by local gas streams in the direct vicinity of the burning surface, or by a nonsteady-state regime.

The mechanisms by which combustion products can penetrate into the pores are also discussed in (15) and conditions were established under which penetration takes place. Deflagration to detonation transitions were studied by Andreyev (2). He discusses the effect of particle size and density on the transition.

An experimental study on the effect of density on the burning velocity of ammonium perchlorate (6) showed that increasing density can either increase or decrease the burning velocity depending on the absence or presence of some admixtures (hexamethyleneteramine, cuprous oxide). A method for determining the density profile during combustion by means of an x-ray absorption method is described (36) and the effect of the density of pyroxiline powder on the burning velocity at 20—30 atm was studied (43).

To summarize, it may be said that the particle size, density, and porosity, which are interrelated properties of the propellant, are factors strongly affecting the combustion characteristics and stability. Soviet research appears to emphasize the following problems: the selection of an oxidizer particle spectrum which yields a minimal pressure vs burning velocity relationship (68); determination of particle size vs burning velocity relationships and their pressure dependence (8, 9, 11); density vs burning velocity relationships and the effect of additives on this relationship (5); the possibility of coating particles (microencapsulation) to make a propellant less susceptible to instability (17); and gas penetration into pores and pore wall ignition (40, 15).

3. THE EFFECT OF TEMPERATURE

The combustion temperature, the initial propellant temperature, and the temperature of the propellant surface are important parameters which affect the burning velocity in the same manner as the pressure and, therefore, temperature fluctuations are directly related to instability phenomena. Soviet researchers have devoted a number of studies to this important subject.

A formula for determining the temperature of the controlling reaction zone, the so called "effective temperature" was derived (12). Another study (67) determined the effect of the gas-phase temperature on the burning velocity of nitroglycerine and pyroxylin powders. An investigation (42) of the dependence of the initial temperature of the propellant on the burning velocity of mixtures of $KClO_4$ with tungsten or zirconium and of pyroxylin powder showed that the heat released in the condensed phase decreases when the initial powder temperature increases. Therefore, it appears that the initial temperature may have a considerable effect on the combustion mechanism and thus be an important factor in assessing instability. The temperature dependence of the kinetic parameters of the condensed-phase reaction was studied (52), and measurements of the flame temperature of PETN, hexogen, and tetryl (57) and of ballistic powders in (38) are described.

4. CONDENSED PHASE REACTIONS

Exothermal condensed-phase reactions in the combustion of solid propellants may be considered to be of importance for evaluating combustion in general and instability characteristics in particular. Soviet investigators have exhibited considerable interest in the role of condensed-phase reactions in propellants in which heat release occurs either predominantly in the condensed phase such as in thermites or both in the condensed as well as the gas phase. A recently published article (34) illustrating the importance of condensed phase reactions deals with a model mixture in which a thermite ($Al + Fe_2O_3$) was diluted with Al_2O_3 in order to lower the combustion temperature and thus avoid the evaporation of aluminum. Such a model mixture can be used for studying condensed-phase characteristics in the complete absence of gas-phase reactions. The burning velocity of these mixtures is independent of pressure and particle size and exhibits a characteristic minimum at a given density. These appear to be significant features of condensed-phase reactions. The model mixtures can also be used for studying the complex relationships between the effects of the gas-phase reactions and those of the condensed-phase.

Several theoretical studies have been devoted to the propagation of the reaction front in the condensed phase. For instance, S. S. Novikov derived formulas for calculating the propagation velocity of a first- and zero-order reaction in the condensed phase (49). He also analyzed two theoretical models describing condensed phase reactions under different conditions (45) and determined the existence of a unique solution of equations describing condensed-phase combustion (46). Another analysis allowing for reaction kinetics yielded a formula for calculating the condensed phase burning velocity (66).

Several experimental studies have also been devoted to this subject. Experiments with mixtures of KClO_4 with metals showed that only 7% of oxide is formed while 30% of the KClO_4 is decomposed in the condensed phase. Therefore, in this system, the reaction in the condensed phase takes place only on the surface of the metal particles and combustion of the oxide-coated metal particles is then completed in the smoke phase (55). Another experimental study with ballistic powders showed that the heat release in the condensed phase increases with increasing pressure (56). A comprehensive study was also made of the heats released in the condensed and gas phases in the combustion of hexogen (37).

To summarize, it may be said that propellants with heat release predominantly in the condensed phase are less pressure dependent and less susceptible to instability than propellants with mainly gas-phase reactions. By increasing the pressure, the conversion in the condensed phase can be increased. The heat release in the condensed phase can also be increased by increasing the initial temperature of the propellant. The finding that oxide coated metal particles are formed in KClO_4 -metal mixtures may be important, since the combustion of such particles in the dispersed phase may be connected with instability.

5. IGNITION CHARACTERISTICS

Ignition characteristics of solid propellants are important from the viewpoint of general combustion theory as well as for practical applications such as starting or restarting of motors. Soviet investigators have devoted several studies to this subject. Studies were made on the ignition with solid bodies (4, 63), a shock wave (27), by hot gases (31, 23) and by radiative energy (69, 26).

To verify the analysis of the ignition of a solid propellant by a solid body presented in (4), an experimental study (23) was made with pyroxylin which was brought into contact with a hot aluminum block. Relationships for the ignition delay time as a function of the initial powder temperature and temperature of the aluminum block were obtained. The ignition of ballistic powders by means of a shock wave was also studied (27). Propellant ignition by a hot gas stream was studied theoretically with emphasis on kinetics and by experiments in which the ignition temperatures and delay times of nitroglycerine-nitrocellulose powder particles were determined in air and argon (23). Another theoretical study (31) of ignition by hot gases was made by V. B. Librovich, who derived a method for calculating ignition parameters. An apparatus for determining ignition delay times in hot gas streams is described in (32). A theoretical study on ignition by light irradiation (69) showed that the burning velocity fluctuates during the transition from ignition to normal combustion. Ignition of gas mixtures with β -radiation was also studied (26). The ignition temperatures of thermit mixtures were determined in (35) and of pure metals, borides, and carbides in (3). All the experimental studies reviewed deal with the ignition of ballistic powders or thermites, but perchlorate mixtures were not investigated.

6. ADDITIVES AND CATALYTIC EFFECTS

The majority of Soviet solid propellant studies on catalytic effects and additives deal with the effects of metal salts on the decomposition rate of perchlorates. Other important studies were made of the effect of light and the combustion products.

An investigation of the effects of Cu, Mn, Co, Fe, and Ni salts and oxides on the decomposition rate of ammonium perchlorate showed that copper compounds are most effective in increasing the burning velocity (60). In another study (61), it was found that Cu, Mn, Co, and Zn carbonates, oxalates, and chlorides accelerate the decomposition of ammonium perchlorate while Fe, Cr, V, and Ni compounds have an inhibiting effect. A study (71) on the effect of heterophase semiconductor impurities (NiO, Cu₂O, ZnO, CdO, and B) on the decomposition of PbN₆, KClO₄, NH₄ClO₄, and AgN₃ showed that the decomposition rate can be varied in the desired direction by using such additives. Their effect can be evaluated from their electronic work function. Another study (64) was made of the effects of Ag, Cu, and Fe salts in low concentrations on the decomposition of ammonium

perchlorate. An investigation of the decomposition of ammonium perchlorate (29) showed that its decomposition rate at a surface temperature of 270°C can be explained by the catalytic effect of combustion products diffusing to the burning surface. A kinetic study of the decomposition of ammonium perchlorate without additives (39) showed that after phase transformation from the orthorhombic to the cubic modification, the decomposition rate is lowered appreciably.

The kinetics of pure metal particle combustion was studied in (19). A study of light irradiation (37) showed that combustion is affected by light both thermally as well as photochemically.

In conclusion, it may be said that great emphasis has been placed on the decomposition characteristics of perchlorates with and without additives and that most of the effects are well known. The studies on the effect of light (28) and of combustion products (46) may be of importance for evaluating combustion characteristics under specific conditions.

7. THEORETICAL STABILITY CRITERIA

Several Soviet investigators have shown great interest in the theoretical derivation of criteria for combustion instability. The predictive value of these criteria is usually limited by the specific assumptions made for the combustion model. Nevertheless, these criteria are of considerable theoretical interest and, in some cases, they may point to conditions which induce instability. Among the more recent studies is a work (51) by B. V. Novozhilov, who used a model with a two-stage combustion process which allows for the condensed-phase, dispersed-phase, and gas-phase reactions. A criterion for the amplification of acoustic high frequency oscillations by the burning surface was derived by a different approach in (25). The effect of the acoustic energy on the mass transfer from a camphor sphere was studied experimentally and theoretically (18). It appears that this investigation may contain basic results which could be of great interest in studying instability as well as the intensification of solid propellant combustion by acoustic energy. A combustion model applicable to liquid as well as solid propellants, which takes into account the formation of foam and aerosol from the molten propellant layer, was developed (33) and used for deriving relationships for the burning velocity of liquid or melting solid propellants. S. S. Novikov derived a criterion in terms of the acoustic admittance of the burning

surface (44). The same author refined the model used in (44) and derived criteria (47) for the acoustic admittance of a burning surface using a model with five regions. In another study (48), he derived criteria on the basis of two specific combustion models.

8. MISCELLANEOUS

This section contains various abstracts dealing with such topics as: the heats of combustion of cyclopentadienylmanganese tricarbonyl (70); of ammonium borane (58); the heat of formation of inorganic ammonium and hydrazonium salts (62); and with the general theory of solid rocket motors (1).

PART II. ABSTRACTS

1. Alemasov, V. Ye. Teoriya raketnykh dvigateley (Theory of Rocket Engines). Moscow, Oborongiz, 1962. 476 p.

This textbook is intended for students specializing in aircraft engines at advanced aviation institutes. It may also be used by engineers in the same field of interest. The author states that while previous textbooks written by Soviet scientists A. V. Bolgarskiy, V. K. Shchukin, A. V. Kvasnikov, G. B. Sinyarev, M. V. Dobrovolskiy, V. I. Feodos'yev, M. I. Shevelyuk, and others describe liquid-propellant rocket engines, the theory of solid-propellant rocket engines is discussed to only a very limited extent. Moreover, there is a lack of textbooks dealing simultaneously with the theory of jet engines operating on various types of fuel; books of this type would be quite useful and economical. The present work describes fundamentals in the calculation and theory of various types of jet engines. An analysis is given of operating processes and the characteristics and parameters of engines utilizing the chemical energy of liquid and solid propellants. Combustion chambers, solid propellant combustion, nozzle characteristics, and steam-gas generation were also covered.

2. Andreyev, K. K. Transition from deflagration to detonation of explosives. Vsryvnoye delo, sbornik no. 52/9, 1963, 130-140.

The differences between burning and detonation of explosives are reviewed, and factors affecting the transition are noted. The acceleration of the burning of granular explosives is discussed, with notes on the effect of particle size and charge density. Secondary solid explosives and the transition of the burning of liquid explosives into an explosion are also covered. The dual effect of pressure upon combustion stability of burning is considered briefly.

3. Arabey, B. G., S. Ye. Salibekov, and Yu. V. Levinskiy.
Ignitability of certain powder materials. Poro-
shkovaya metallurgiya, no. 3, 1964, 109-113.

The ignition temperature and the nature of combustion of some refractory metals, carbide, and boride powders were determined in an effort to establish safe handling procedures for these materials. The tested powders had a grain size of 3—10 μ , which is the size most frequently used in powder metallurgy. Heating was done either in a furnace in an air atmosphere or by a point source (a nichrome spiral) brought into contact with the powder. It was found that the smaller the powder grain size, the more pyrophoric the powder. In the furnace, at grain sizes tested, powders of zirconium ignited at 270°C, niobium at 290°C, tantalum at 290°C, molybdenum at 310°C, tungsten at 410°C, titanium at 520°C (with a flash), nickel at 470°C, iron at 470°C (flash at 630°C), and boron at 570°C (with a flash). With a point heat source, the ignition temperatures were generally higher than those obtained with the furnace, the difference varying from 10°C for boron to 220°C for molybdenum. Only iron ignited at 350°C. Chromium and nickel remained intact at point

source temperatures up to 1000°C. Borides (TiB_2 , ZrB_2 , CrB_2 , HfB_2 , SiB_6 , B_4C) did not ignite under 1100°C; zirconium, hafnium, niobium, and tungsten carbides had ignition points ranging from 760 to 1000°C.

4. Averson, A. E., V. V. Barzykin, and A. G. Merzhanov.
Relationships for ignition of condensed explosives with
ideal heat transfer at the surface and with allowance
for burnup. Inzhenerno-fizicheskiy zhurnal, v. 9,
no. 2, 1965, 245-249.

An analysis is made of the ignition process taking place when a solid propellant is brought into contact with a solid heat source. It was assumed that a homogeneous, first order reaction takes place in the condensed phase in the presence of nonsteady-state heat transfer at the surface from the source. No allowance was made for phase transformations in the interior or on the surface of the propellant, individual kinetic and physical stages, dispersion of the condensed medium, etc. The propellant was assumed to be semi-infinite. The surface temperature of the source T_0 was assumed to remain constant. The spatial and temporal profiles of the temperature and conversion were obtained by electronic computation taking the difference between the heat source and the propellant temperatures, $\beta = RT_0/E$ and $\gamma = c_p RT_0^2/QE$ as parameters, where c is the specific heat; ρ , the density; E , the activation energy; R , the gas constant; and Q , the

specific heat release. It was found that with a small γ (weak ignition source), the ignition process is self-accelerating and resembles a thermal explosion. As γ approaches the value of γ_{com} (γ during combustion), two different regimes with high conversion can be established depending on whether $\gamma > \gamma_{com}$ or $\gamma < \gamma_{com}$. The following additional conclusions are made: at low conversion, the reaction may be assumed to be of zero order. The ignition delay times calculated by a formula previously developed by Zel'dovich are in some cases about 50% lower than the actual values. Therefore, this formula cannot always be used. The width of the reaction zone under a normal regime is practically independent of the temperature difference between the source and the propellant.

5. Bakhman, N. N., A. F. Belyayev, G. V. Lukashenya, and D. P. Polikarpov. The relation between the combustion rate of ammonium perchlorate and its density. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 1, 1964, 131-134.

The combustion rate (u cm/sec) of compacted systems depends on the relative density δ of the sample, where δ is equal to the $\rho/\rho_{\max}$ ratio. Here ρ gm/cm³ represents the actual, and $\rho_{\max}$ the potentially possible density of the given sample. The shape of the u curve depends, in turn, upon the conditions under which the reaction takes place and on the existing heat losses. The present investigation was performed on compacted ammonium perchlorate in a constant pressure tank in an atmosphere of nitrogen. The first series of tests was conducted on a charge 10 mm in diameter encased in an inert coat of cement-phosphate or glass. It was observed that low values of relative density δ diminished the combustion rate; the combustion even became incomplete at $\delta = 0.75-0.65$. In order to assess the role of heat loss, the second series of experiments was carried out in plexiglass containers with a 6-mm internal diameter. The result showed that with a

lower δ , the combustion rate was increased. In the third series of experiments, 2% hexamethylenetetramine were added to the ammonium perchlorate in a plexiglass casing. It was found that here a lowering of δ caused even a slight increase in the combustion rate. In the fourth series, 2% Cu₂O was added as a catalyst, which accelerated the reaction rate and reduced the zonal width of the reaction. The fifth series was conducted with pure ammonium perchlorate at a higher initial temperature. This caused the combustion rate to increase. The incorporation of small amounts of asphalt had an inhibitory effect on the combustion rate, while larger quantities enhanced it.

6. Bakhman, N. N., and V. S. Nikiforov. Condensed mixtures with strong dependence of the burning rate on the dispersion of the components. Zhurnal fizicheskoy khimii, v. 38, no. 1, 1964, 41-46.

The burning rate u of condensed mixtures with a very small coefficient of mass transfer A is governed by the particle size d of the components. For mixtures with a large A , the function $u(d)$ is small. The ratio between u for mixtures with the smallest $d(u_1)$ and u for mixtures with the largest $d(u_2)$, $\delta = u_1/u_2$ was calculated for mixtures containing 80—95% W and 5—20% $KClO_4$ and mixtures containing 25% Al and 75% Fe_2O_3 . For W and Al, δ decreased as the pressure p increased from 5 to 100 atm. By varying the diameter of the metal particles, u can be varied in W + $KClO_4$ mixtures by a factor of 40—50 and in Fe_2O_3 , by a factor of 20 to 30. In mixtures in which both components are gasified, u increased only 2—4 times.

7. Bakhman, N. N., and Yu. A. Kondrashkov. Burning of three-component condensed mixtures. Zhurnal fizicheskoy khimii, v. 37, no. 1, 1963, 216-219.

The effect of the particle size of metal powders added to two-component mixtures on the linear burning rate was studied in $KClO_4$ -asphalt mixtures containing 13.1% Al, Ti, W, or Zr powders with particles of 2.5 to 190 μ . Large particles (Al and W, 190 μ) decreased the burning rate by only about 5—15% compared with the rate of the nonmetallized mixtures. This is attributed to the fact that large particles burn far behind the main combustion zone, so that heat from the metal combustion is not transmitted to the fresh mixture. On the other hand, the decrease of combustion temperature from heat consumed in the heating and phase transformation of the metal is not large. With decreasing metal particle size, the heat consumed in heating them increases. At the same time, the heat flux from the metal combustion to the main combustion zone also increases. Owing to these factors, as the particle size decreases, the burning-rate versus particle-size curve passes through a minimum. Because small particles

burn in front of the main combustion zone, the burning rate does not increase further when the particle size is decreased below a certain limiting value. With medium-size particles, the effect of the metal on the burning rate decreases with increasing pressure, because the gas reaction rate increases more rapidly with pressure than the combustion rate of the metal. The study was made at the Institute of Chemical Physics, Academy of Sciences USSR.

8. Bakhman, N. N., and Yu. A. Kondrashkov. Model of a burning front of condensed mixtures. IN: Akademiya nauk SSSR. Doklady, v. 142, no. 2, 1962, 377-379.

A model of a burning front which takes into consideration the inhomogeneity of the mixture and permits the derivation of an equation for $u(d)$ (u = burning rate, d = particle size) is studied. For $d \leq d_{min}$, the burning front is plane. With increasing d , protrusions form at the burning front. The burning rate is assumed to be kinetically controlled. The values calculated by the derived equations agreed well with the experimental data.

9. Bakhman, N. N. Diffusion combustion regime in the presence of condensed reaction products. Zhurnal fizicheskoy khimii, v. 39, no. 8, 1965, 1860-1862.

The effects of particle size d on the pressure dependence of the burning velocity u of solid combustibles is examined. Previous experiments (N. N. Bakhman, V. S. Nikiforov. Zh. fiz. khimii, 38, 41, 1964) have shown that with $W + KClO_4$ and $Al + Fe_2O_3$ mixtures, the burning velocity of mixtures with large particles is less dependent on pressure p than that of mixtures with small particles. These findings contradict the Zel'dovich theory (Ya. B. Zel'dovich, Zh. eksperim. i teor. fiziki, 12, 498, 1942) which assumed that when the reaction takes place in the gas phase, it is found that $u \sim \sqrt{p/d}$ for small particles and $u \sim d^{-1}$ for large particle mixtures. Therefore, the dependence of burning velocity on pressure should be more pronounced in mixtures with large particles. Such a relationship has been observed for $KClO_4$ + graphite mixtures. However, the contradictory behavior observed with the $W + KClO_4$ and $Al + Fe_2O_3$ mixtures suggests that the reaction does not take place in the gas stream, but that the oxidizer diffuses through a condensed liquid

layer of combustion products such as KCl , WO_2 , Fe , Al_2O_3 , etc. Five different mechanisms can exist depending on whether the oxidizer decomposes or remains unchanged. For the cases studied, the following two mixed mechanisms are suggested. When the combustible particle size is sufficiently small and the contact surface is sufficiently large, the oxidizer diffuses the combustible without decomposition. Therefore, $u_p \neq f(p)$, where ρ is the density. When d is sufficiently large, the oxidizer is first decomposed and then diffuses in the form of oxygen to the combustible. In this case, $u_p = \sqrt{p}$. When the fuel particle diameter is small compared with that of the oxygen bubbles and the jets in the liquid phase, $u_p \neq f(p)$. When the fuel particles are large compared with the bubbles or jets, oxygen transport takes place also by diffusion in the condensed phase and $u_p \sim \sqrt{p}$. The proposed mechanism satisfactorily explains the observed data.

10. Bakhman, N. N. On the calculation of the pressure rise on a combustion front. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 1, 1965, 106-108.

The pressure difference between the surface of a burning condensed substance and the surrounding volume is calculated, with special attention devoted to after-burning, when the heat release takes place partially or completely in the gaseous phase, or when the rate of outflow of gaseous reaction products approaches the speed of sound. The calculation is based on the conservation laws. Numerical estimates are presented for real condensed substances confined to not too short a shell, under the assumption that the gas flow and motion of the combustion front are uniform. The minimum pressure on the charge needed to support the reaction is also estimated, and is found to be 4—8 mm Hg in the case of fulminate of mercury, and about 4 atmospheres in the case of lead styphnate. It is much lower for secondary explosives and powders (~ 1 mm Hg for pyroxiline powder). If the combustion front is not uniform, the pressure drop is smaller.

11. Bakhman, N. N. The cause of the anomalous dependence of the burning velocity on the composition of the components. Zhurnal fizicheskoy khimii, v. 39, no. 3, 1965, 764-766.

As a rule, the burning velocity u of condensed systems increases as the particle size of the components decreases. However, with NH_4ClO_4 -polystyrene mixtures at high pressures, the u of mixtures with small ($\sim 15 \mu$) particle size of the oxidant is lower than for mixtures containing 50% coarse (320—410 μ) and 50% fine ($\sim 50 \mu$) NH_4ClO_4 . Experiments with gelatinization of the mixture (by treating with dichloroethane for 24 hr and drying) showed that in the pressure range of 5—100 atm gage, the u of the gelatinized mixtures with small particle size of the oxidant was higher than of that with mixed (coarse and fine) particle size of the oxidant, i.e., the dependence of the burning velocity on the particle size was normal. The burning velocity is not controlled by the entire burning zone, but by only a small area of it, an effective burning zone near the surface, which decreases with pressure. In this zone, the comparatively smaller (15 μ) oxidizer particles disappear faster than the fuel particles (100 μ) and combustion

takes place in an oxidizer-rich regime. The gelatinization of the mixture increases the fuel particle size of small particles considerably, but the size of large particles only slightly. Thus, the gelatinized mixture exhibits a normal relationship between burning velocity and particle size. It is concluded that mixtures having the maximum burning velocity at an excess of fuel may exhibit an anomalous dependence of the burning velocity on the particle size. The use of large instead of small oxidizer particles can increase rather than decrease the burning velocity.

12. Belyayev, A. F., and G. V. Lukashenya. Effective temperature of burning of some explosives. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 6, 1963, 114-120.

Using the previously defined temperature coefficient of the rate of reaction, $\beta = d \ln u / d T_0$, and the relationship between the burning velocity and the activation energy, the following equation was derived for calculating the temperature of the principal stage of reaction in the burning of explosives T_e , called the effective temperature:

$$T_e \approx \sqrt{\frac{E}{2R\beta}},$$

where E is the activation energy. Data on the effective temperatures are tabulated for nitroglycerol, tetryl, nitroglycerin, methylnitrate, hexogen, and trotyl. At $E = 30-50$ kcal/mole and $\beta = 10-15 \cdot 10^{-3}$ /degree, $T_e = 500-900^\circ\text{K}$, which indicates that the principal reaction occurs in the condensed phase. At $\beta = 2.5 \cdot 10^{-3}$ or less, $T_e = 2000^\circ\text{K}$ or more, indicating that the principal reaction occurs in the gaseous phase. For the explosives studied, at atmospheric pressures, T_e (1400

to 1800°K) is considerably lower than the maximum temperature at high pressures, and for the majority of explosives, it is lower than the final temperature. For ammonium perchlorate, β was found to be practically the same under different conditions ($\sim 5.8 \cdot 10^{-3}$) and $T_e = 1100^\circ\text{K}$, which is very close to the temperature measured. This is in agreement with the previously postulated view that the principal reaction in the burning of ammonium perchlorate takes place in the gaseous phase. With the addition of a combustible to ammonium perchlorate and with increasing burning rate, β decreases and T_e increases.

13. Belyayev, A. F., S. A. Tsyganov, and Ya. B. Zel'dovich. Mechanism of burning of smokeless powder at elevated pressures. IN: Akademiya nauk SSSR. Doklady, v. 157, no. 2, 1964, 378-380.

The burning velocities of smokeless powder, PETN, and a mixture of PETN and 5% finely ground charcoal were determined as a function of pressure, $V(P)$, in a constant-pressure bomb in compressed nitrogen at 10 to 110 atm. The results are shown in Fig. 1. The curves

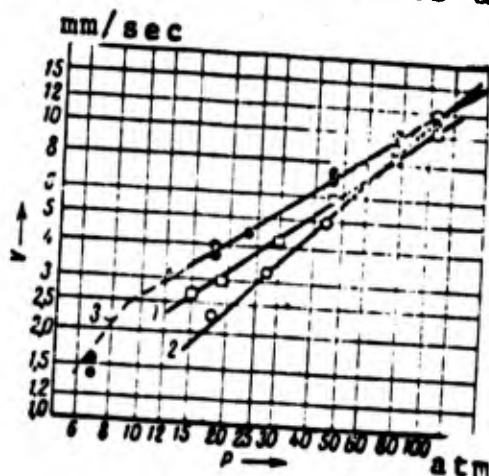


Fig. 1. Dependence of burning velocity on pressure

1 - Smokeless powder;
2 - PETN; 3 - PETN + charcoal.

of burning velocity vs pressure show that both smokeless powder and the mixture of PETN and charcoal have higher burning velocities than PETN alone. Photomicrographs of the burning of the PETN-charcoal mixture showed the existence of a narrow layer of glowing solid particles located about 0.1 mm from the surface of the specimen. The burning of smokeless powder at pressures above 10 atm is a heterogeneous process. In the initial stage, a dispersed system of gaseous decomposition products and solid particles is formed; in a later stage, exothermic reactions of the gaseous products take place on the surface of the glowing solid particles, which accelerate the reactions of the gaseous products; this stage becomes the controlling factor for the burning velocity of the explosive. Experiments were also carried out with the burning of other explosives (trotyl, hexogen, and a mixture of trotyl with ammonium nitrate) containing 3-6% charcoal. These experiments also confirmed that the presence of charcoal accelerates the burning of explosives, owing to the formation of a dispersed system ("smoke") with glowing solid particles.

14. Belyayev, A. F., Yu. A. Kondrashkov, G. V. Lukashenya, A. K. Parfenov, and S. A. Tsyganov. Flame combustion of model mixtures of oxidizer with fuel. Nauchno-tekhnicheskiye problemy goreniya i vzryva, no. 1, 1965, 25-30.

The relationship between the burning velocity u and pressure p of composite propellants was studied at subatomic pressures. Ammonium perchlorate-trotyl, potassium, ammonium perchlorate-asphalt, ammonium perchlorate-paraformaldehyde, and ammonium perchlorate-polystyrene were ground to 20 to 40 μ and intensively mixed and compacted to 98% of the maximum density. Although the propellants had different fuels, oxidizers, and polymer binders, the u -vs- p relationships were linear. Therefore, it appears that systems which contain sufficiently fine components and fuels which can be gasified by decomposition, pyrolysis, or evaporation, give linear u -vs- p relationships at subatmospheric pressures. The experimental results together with an evaluation of burning velocities at higher pressures, obtained previously, indicate that the following four regions exist: 1) a low-pressure region characterized by a plane flame front up to about 2 atm ($v = 1$); 2) the

region of transition from a plane to a multiflame front with a nonlinear u -vs- p relationship ($v < 1$) at 2.5 to 3 to 100—250 atm; 3) a high-pressure region characterized by a multiflame front but with a linear u -vs- p relationship from 100—200 to 1000—1500 atm; and 4) a region above 1500 atm ($v < 0.3$ — 0.4). Multiflame fronts consist of flames which propagate along the fuel-oxidizer boundaries into the propellant.

15. Bobolev, V. K., A. D. Margolin, and S. V. Chuyko. Mechanism of the penetration of combustion products into pores of explosive charges. IN: Akademiya nauk SSSR. Doklady, v. 162, no. 2, 1965, 388-391.

The following two mechanisms of the penetration of combustion products into the pores of an explosive charge are postulated and experimentally substantiated: 1) forced penetration, which depends on the outer pressure far from the burning surface and which is not connected with the combustion process itself, but with increasing outer pressure; and 2) spontaneous penetration, which is connected directly with the combustion process and occurs under the conditions of nonsteady-state combustion near the charge surface. This is attributed to surface and gas-flow nonuniformities. The forced penetration takes place when the velocity of the penetrating gas v_g relative to the pores is higher than the linear burning velocity u , $v_g - u > 0$. For the case when the gas pressure P over a pore increases with a velocity dP/dt ,

$$v_g = \frac{H_0}{P} \frac{dP}{dt} \frac{T_g}{T_0},$$

where H_0 is the height of the pore, T_0 is temperature of the pore wall far from the inlet, and T_g is the temperature of the penetrating gas. Under decreasing pressures, the combustion gases penetrate the pore by the spontaneous mechanism. The theory was verified by experiments with a model pore, a gap (40 mm long and about 0.1 mm wide) between a hexogen charge and a plexiglass plate. The charge was burned in a bomb under controlled nitrogen pressure. The pressure change was registered on an oscillograph, and the combustion process was recorded by high speed photography through the plexiglass plate. The combustion gases penetrated the pore when the initial pressure in the bomb exceeded about 25 atm. The penetration rate increased with pressure. A detailed analysis of the experimental data is given.

16. Bobolev, V. K., A. P. Glazkova, A. A. Zenin, and O. I. Leypunskiy. A study of the temperature distribution in the combustion of ammonium perchlorate. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 3, 1964, 153-158.

To determine the temperature distribution, two types of thermocouples (W + Re—W + Re, 5 and 20% Re) were used: in one case, the cross section of the wire is circular, 15 and 30 μ in diameter, and in the other case, the wire is a ribbon, 3.5 and 7 μ thick. The perchlorate was compressed to obtain samples with a specific gravity of 1.93—1.94 cm³. The experiments were performed in nitrogen under 40—350 atm. The observed temperature profiles showed the existence of two pressure ranges for the combustion: a steady combustion at $60 < p < 150$ atm, and an unsteady combustion at $160 < p < 350$ atm. Unstable combustion is characterized by a periodic change in the temperature (period of 50 msec and an amplitude of 500°C) and when the pressure increases, by a decreasing heat release in the condensed phase. It is suggested that the combustion mechanism changes with the pressure change and that the diffusion of the combustion products from

the gaseous combustion zone to the condensed phase has a catalytic effect on the combustion process. A hypothesis is advanced to explain the observed decrease in the burning velocity with increasing pressure at $p > 150$ atm.

17. Bobolev, V. K., I. A. Karpukhin, and S. V. Chuyko. Combustion of porous explosive charges. Nauchno-tekhnicheskiye problemy goreniya i vzryva, no. 1, 1965, 44-51.

Previous experiments have shown that the transition from deflagration to detonation in porous propellants is connected with an unbalanced formation and removal of gas from the pores. The transition from deflagration to detonation in hexogen charges of 50—360 μ particle size, with and without the addition of paraffin wax, was studied by pressure recordings and high-speed photography. Normal combustion took place under constant pressure for about 3 sec, then the burning velocity increased, and gradual transition to a perturbed combustion regime occurred, characterized by luminosity pulsations. The lengths of the periods of low luminosity increased with increasing particle size. The following mechanism is proposed. Normal combustion takes place only when the hot gases penetrating into the pores do not heat the grain to the gasification temperature to a depth exceeding that of the thermal layer. If this depth is exceeded, transi-

tion takes place. Paraffin wax acts as a thermal barrier in the penetration of combustion products into the pores, and thus retards the transition from deflagration to detonation.

18. Burdukov, A. P., and V. Ye. Nakoryakov. Mass transfer in an acoustic field. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 2, 1965, 62-66.

It is known that the burning rate of liquid or solid fuels increases in the presence of acoustic oscillations. Acoustic oscillations are also used for intensifying chemical processes. However, the mechanism of mass and heat transfer in the presence of oscillations has not been studied sufficiently. In the present study, an analysis of mass transfer in an acoustic field is presented. It was assumed that the sphere is immersed in a medium perturbed by a plane acoustic wave, the density of the medium remains constant, the sphere is rigid, the gas viscosity and the diffusion coefficient are independent of the concentration field, and the wavelength of the acoustic oscillations is smaller than the radius of the sphere ($\lambda/R \gg 1$). The following solution was obtained for $s/R \ll 1$ (s is the displacement amplitude of the particles of the medium in the flat acoustic wave): $N_d = 1.3B/\sqrt{\omega D}$, where N_d is the Nusselt number based on the sphere diameter; B , the oscillation amplitude; ω , the frequency; and D , the diffusion coefficient. The theoretical results were

verified by experiments with camphor spheres 3.5 to 10 mm in diameter in an acoustic field of 11.5—18-kc frequency and 150—163-db intensity. Steady secondary flows previously described by Abrade and Holstmark were found to be the controlling factor for mass transfer. When $s/R \gg 1$, which applies to pulsating combustion chambers, the mass transfer may be considered to be quasi-steady-state, and for this case we obtain $N_d = 0.259P^{1/3}(Bd/v)^{0.6}$.

19. Fedoseyev, V. A. Combustion kinetics of dispersed metal fuel. IN: Akademiya nauk UkrSSR. Institut tekhnicheskoy teplofiziki. Teplofizika i teplotekhnika (Thermophysics and heat engineering). Kiev, Naukova dumka, 1964, 160-162.

The combustion kinetics of magnesium particles were studied by a method based on the injection of particles into a high-temperature airstream and on a photometric evaluation of the traces of the burning particles. Six magnesium powder fractions with different particle size distributions were used to obtain plots of the mass m , radius r , and surface S of a particle as a function of time. The relationships m vs t and r vs t were found to be curves, but S vs t was a linear function. The relationship $dS/dt = \text{const}$, termed Sreznevskiy's law, was found to hold for spherical particles of any metal. For rod-, spiral-, or petal-shaped particles, the law does not hold and $dS/dt \neq 0$. Detailed investigations of the combustion mechanism showed that spherical particles are first covered with an oxide film in the preflame zone, and then as the vapor pressure inside the film increases, the film bursts and

the metal vapors ignite. Elongated particles ignite at the point with the smallest cross section; from there, the flame spreads gradually over the entire particle. In this case, the kinetic characteristics are more complicated and depend on the particle size.

20. Fur, Z. I. Substantiation of the pressure dependence of the burning velocity in the relaxation theory of combustion propagation. *Inzhenerno-fizicheskiy zhurnal*, v. 8, no. 4, 1965, 451-455.

In the previously postulated relaxation theory of combustion propagation in heterogeneous exothermic systems (Z. I. Fur, *Zhurnal fizicheskoy khimii*, v. 34, 1960, 611; 1299), the pressure dependence of the burning velocity was attributed to the dependence of the pressure on the temperature on the condensed phase-gaseous phase interface. However, this suggestion was not substantiated. This problem was investigated again and new, more accurate equations were derived for the burning velocity in heterogeneous exothermic systems. Analysis of the new equations showed that the pressure dependence of the burning velocity is a part of the relaxation mechanism of the propagation, and there is, thus, no need for its substantiation. It was found that v may vary between 0.25 and 0.38 instead of 0 and 0.38, as claimed in the author's previous work. It is also shown that in the case of a combustible mixture of low mechanical strength, the combustion propagation may be independent of pressure.

21. Glazkova, A. P. Effect of pressure on the combustion rate of ammonium perchlorate. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 5, 1963, 121-125.

The study of the process of self-spreading intramolecular oxidation of ammonium perchlorate AP was conducted in bombs in an atmosphere of nitrogen at pressures up to 1000 atm. The combustion rate of ammonium perchlorate was recorded by the photographic technique described in an earlier paper by A. P. Glazkova and I. A. Tereshkin (O zavisimosti skorosti gorennya vzryvchatykh veshchestv ot davleniya. Zh. fiz. khim. 1961, 35, no. 7, 1622). Analytical grade ammonium perchlorate was dried to constant weight and pressed into small sticks having a specific gravity of 1.93—1.94 gm/cm³. It was found that the combustion of a stick 5 mm in diameter dies out at 270 atm, while one with a diameter of 7 mm continues to burn, which may at first glance be explained by an insufficient generation of heat by the smaller stick to overcome the heat losses. Such a point of view seems to be supported by the observation that the 5-mm AP stick had not yet started burning at 50 atm, while the 7-mm stick began to burn even at 30 atm. The photographs revealed that at

140 atm, the combustion of AP is stable with only separate local flashes on the flame front, while at 200—350 atm the luminosity becomes weaker and the combustion acquires a pulsating character. Experiments conducted with AP sticks encased in plexiglass containers or glass tubing or coated with perchlorovinyl lacquer at pressures below 500 atm brought out the insignificant role played by loss of heat on the AP combustion rate. Similar studies conducted at pressures within the 500—1000 atm range revealed that at 1000 atm, the combustion rate of AP in plexiglass tubes amounted to 14 gm/cm² per sec, while in perchlorovinyl tubes its rate is only 9 gm/cm² per sec. This may be due to some kind of interaction taking place between the AP and the substance of the casing.

22. Gostintsev, Yu. A., and A. D. Margolin. Nonsteady-state powder combustion under the action of pressure pulses. Nauchno-tekhnicheskiye problemy gorennya i vzryva, no. 2, 1965, 69-75.

An analysis was made of the nonsteady-state combustion of solid propellants induced by rectangular or triangular pressure pulses. Combustion of a semi-infinite charge was analyzed on the basis of the Zel'dovich theory of powder combustion. The nonlinear equations of heat conduction were solved through the use of integral relationships. As a result, a diagram was obtained which shows the regions of flame extinction as a function of the intensity and duration of the pressure pulses. The optimum condition for extinction exists when the duration of the pressure pulse is of the same order of magnitude as the thermal relaxation time of the heated propellant layer. With very short pressure pulses, the theoretical results do not correspond to the experimental results because the processes in the gas and condensed phases are not quasi-steady-state as assumed in the analysis.

23. Grigor'yev, Yu. M., E. I. Maksimov, and A. G. Merzhanov. Relationships for the ignition of homogenous explosive particles in hot gas. Nauchno-tekhnicheskiye problemy gorennya i vzryva, no. 1, 1965, 93-102.

A theory of the kinetics of decomposition of nonvolatile explosive particles in a hot gas has been developed on the basis of a simple model. The model assumes that the exothermal reaction takes place on the surface of the condensed particle which does not undergo phase transformation or change of size in the pre-explosion period, that the spherical explosive particle enters a cavity filled with hot gas, that heat transfer inside the particle takes place by conduction and external heat transfer by conduction and radiation, and that convective transfer is absent. The analysis yielded expressions for the temperature profile in the gas and inside the particle, for the time required to heat the particle, and for the induction period. To verify the theoretical relationships, experiments were made with nitrocellulose-pyroxylene powder particles (50-150 μ particle size) in horizontal and vertical glass tubes. The ignition temperatures of 50 μ particles were 255°C.

in air and 246°C in argon. This difference is attributed to the higher thermal conductivity of argon. Ignition delay times determined as a function of temperature were in good agreement with the theory.

24. Istratov, A. G., V. B. Librovich, and B. V. Novozhilov. An approximate method in the theory of the nonsteady-state burning rate of powder. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 3, 1964, 139-144.

Analytical expressions are derived for calculating the rates of nonsteady-state burning of powder when combustion is dependent only on the pressure and temperature gradients at the surface of the condensed phase. An instant pressure change and an exponential pressure change are considered. The theory is in good agreement with experimental results.

25. Karakozov, G. K., and G. V. Rossikhin. The mechanism of intensification of acoustic oscillations by the burning surface of a solid fuel. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 4, 1964, 135-136.

The conditions under which acoustic oscillations are intensified by the burning surface in the combustion of solid propellants were analyzed (see Fig. 1). A layer is considered which is bounded by the surfaces (-) and (+). The distance between the surfaces is constant. The surface (-) is situated in the gas phase at a point where the reaction is completed. The change in parameters to the left of this surface is considered to be isentropic. To the right of surface (+), the gas is ideal and has a fixed chemical composition. Curve 1 shows the density distribution in the layer at steady-state combustion. Curve 2 represents the adiabatic density distribution in the presence of a rapid pressure increase caused by passage of the acoustic wave front. Curve 3 represents the steady-state density distribution at a new pressure. The following criterion was derived for the intensification of high-frequency acoustic oscillations:

$$\frac{p}{m\tau} \left\{ \left(\frac{\partial M}{\partial p} \right)_{\infty} - \left(\frac{\partial M}{\partial p} \right)_0 \right\} + \frac{k-1}{k} - \left(1 - \frac{p_+}{p_-} \frac{p}{p_- c_-^2} \right) > 0,$$

where p is the pressure, m is the mass flux, τ is the characteristic time for redistribution of the parameters

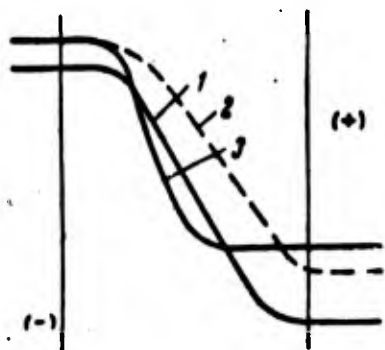


Fig. 1. Density distributions between surfaces (-) and (+)

in the considered layer during relaxation, M is the mass in the considered layer, ρ_- and ρ_+ are density fluxes in the surfaces (-) and (+), respectively, k is the adiabatic exponent of combustion products, and c_- is the acoustic velocity in the surface (-). The subscript ∞ refers to the condition $\omega\tau \rightarrow \infty$, where ω is the frequency.

26. Khudenko, B. G. The conditions of ignition in nonthermal activation of combustible mixtures. IN: Izvestiya vysshikh uchebnykh zavedeniy. Aviatsionnaya tekhnika, no. 2, 1965, 121-131.

A theoretical analysis yielded criteria for determining the intensity of the radiation source required to effect the ignition of a combustible mixture. The calculations were made for a radiation source mounted on the wall of a tube or on a rod placed in the center of the tube containing the combustible mixture. Criteria in terms of effective collision numbers were derived for thermal and chain ignition. Application of the criteria to previous experimental data on the ignition of propane-air and butane-oxygen mixtures with β -radiation sources showed good agreement between experimental and theoretical data. The effect of the radiation source intensity on the burning velocity is also discussed.

27. Kiselev, Ye. Ye., A. D. Margolin, and P. F. Pokhil. Shock-wave ignition of gun powder. Fizika goreniya i vzryva, no. 4, 1965, 83-84.

Ignition of nitroglycerin and nitrocellulose powder by a shock wave was studied in a shock tube 4.7 m long and 41 mm in diameter. The tube was divided by a copper diaphragm into a low-pressure chamber filled with air and a high-pressure chamber filled with compressed nitrogen. The pressure in the shock wave was 3-25 atm and the temperature was 500-1500°K. The ignition delay decreased as the pressure and gas temperature in the reflected shock wave increased. At a gas temperature of about 1000°K, the ignition occurred within milliseconds. The effect of the powder surface temperature and the surface structure on the ignition process was discussed. It was suggested that charges with rough surfaces ignite at much lower surface temperatures than charges with smooth surfaces. This was proven by experiments with specially prepared smooth-surface charges. The surface of the nitroglycerin and nitrocellulose powder was moistened with acetone and pressed against a glass plate. After several days, the powder charge was separated and ignited in the

shock tube. Under the same conditions, the smooth-surface charges did not ignite even at temperatures 200—300°K higher than the ignition temperature of charges with the usual rough surface; however, a small scratch on the smooth surface leads to ignition of the charges. Thus, the ignition of powder charges is greatly dependent on the state of the charge surface. Microprotrusions on the surface are heated much faster than the whole surface and considerably decrease the surface temperature at which the ignition occurs.

28. Konev, E. V. The effect of light irradiation on the burning velocity of powder. Nauchno-tekhnicheskiye problemy gorennya i vzryva, no. 2, 1965, 76-82.

Previous experiments by the author indicated that light irradiation affects the combustion of ballistite H not only thermally but also photochemically. To study this phenomenon, the burning velocity of ballistite H samples, 20 mm long and 7 mm in diameter, was measured as a function of the incident light-flux density and the initial temperature. By comparing the burning velocities obtained at light flux densities of 0—4 kcal/cm²·sec and at initial temperatures of -78 to 130°C, it was found that light irradiation emitted from a carbon source with a temperature of 1700—2000°K has only a thermal and not a photochemical effect. The energy loss by light absorption in the combustion products of ballistite H and by reflection from its surface amounted to 29% of the original light energy.

29. Leypunskiy, O. I. Possible effect of the diffusion flow of reaction products from a flame on condensed-phase decomposition. IN: Akademiya nauk SSSR. Doklady, v. 155, no. 4, 1964, 897-899.

The hypothesis is advanced that the decomposition of the condensed phase of a propellant can be accelerated by diffusion of catalytically active molecules from the flame to the propellant surface. This hypothesis could explain the decomposition rate of 3 mm/sec of NH_4ClO_4 at a surface temperature of 270° , since decomposition kinetics cannot account for such a large rate at this low temperature. Approximate calculations were made for the concentration of decomposition products in the gas phase near the propellant surface and for the diffusion flow of products from the flame to the surface. The diffusion is expressed as the ratio of the diffusion rate to the mass rate of burning. For nitroglycol and black powder with surface temperatures of 200° and 320° , these ratios are 0.15 and 0.039, respectively. These values are not believed to be inconsistent with the proposed hypothesis.

30. Leypunskiy, O. I., V. I. Kolesnikov-Svinarev, and V. N. Marshakov. The unsteady rate of powder combustion. IN: Akademiya nauk SSSR. Doklady, v. 154, no. 4, 1964, 907-909.

The unsteady burning rate u_u of black powder can be detected by determining the rate of pressure change dp/dt . The powder, with a surface area s and density ρ , is burned in a vessel. The unsteady u_u and steady u_s burning rates are related by the following equation from which u_u may be determined:
$$u_u - u_s = (f/V\rho s) dp/dt$$
where f is the energy of the powder and V , the volume of the vessel. An unsteady burning rate results from changes in heat flow at the powder surface, which occur during rapid pressure changes. Under a given pressure, the unsteady rate does not have a specific value, but depends on the previous burning history of the powder.

31. Librovich, V. B. Ignition of powders and explosives. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 6, 1963, 74-79.

The ignition of solid propellants or explosives by a hot gas stream is analyzed theoretically, with the assumption that ignition takes place under the following conditions: 1) the surface temperature attains the value established under a steady-state combustion regime (T_*); 2) a critical temperature gradient near the surface is established to enable flame formation; and 3) the gasified products are ignited. The problem is analyzed for cases in which the heat flux to the propellant is either low or high, according to the conditions

$$\alpha(T_r - T_*) \lesseqgtr \left| \left(\lambda' \frac{\partial T}{\partial x} \right)_* \right|,$$

where T_r is the hot gas temperature, α is the heat transfer coefficient, λ' is thermal conductivity, and $(\partial T / \partial x)$ is the temperature gradient. At low heat fluxes, the powder ignites immediately when the surface temperature reaches T . At high heat fluxes, the

attainment of T_* is not sufficient for ignition, since flame formation is not possible owing to the high temperature gradient. However, as a result of heat removal by gasification, the temperature gradient decreases gradually to the critical value and ignition occurs. Formulas and graphs in terms of dimensionless parameters are derived for determining the ignition parameters and the conditions under which ignition is possible. It is noted that by the intensification of the heat flux from the gas to the propellant, the ignition time cannot be reduced below a minimum value. Therefore, an optimum heat regime must be observed to obtain a minimum ignition time. The transition from ignition to steady-state combustion is considered, and it is shown that at low heat fluxes and propellant temperatures, steady-state combustion is impossible and short duration ignition flashes occur. The method is used for calculating the ignition parameters of nitroglycol with a gas stream of 1273°K. T_* and T_{com} are taken as 473°K and 1650°K, respectively (T_{com} is the combustion temperature). The calculations yielded

the following values:

$$\left| \left(\lambda \frac{\partial T}{\partial x} \right)_* \right|,$$

4.59 cal/cm²·sec; minimum ignition time, 0.31 sec;
thickness of the gasified layer prior to combustion,
3·10⁻³ cm; heat required for ignition, 4.62 cal/cm².

32. Lisitskiy, V. I., and A. G. Merzhanov. Ignition of condensed substances by the flow of hot gases. Nauchno-tekhnicheskiye problemy gorenija i vzryva, no. 2, 1965, 62-68.

Previous studies of the ignition of condensed explosives by the flow of hot gases have not accounted for heat transfer. Therefore, a new apparatus was designed in which the heat transfer between the explosive and the gas is measured under controlled conditions. Ignition of cylindrical charges of pyroxylin No. 1, 0.06 to 1.8 cm in diameter d and with a density $\rho = 1.5$ g/cm³, by the flow of hot gases (air, nitrogen, argon, or carbon dioxide) was studied at gas temperature $T_0 = 250-370^\circ\text{C}$, gas velocity $u = 90-270$ cm/sec, $Re = 150-550$, and an ignition delay time $t_3 = 15-95$ sec. The ignition delay was determined as a function of T_0 , the temperature of the pyroxylin charge T_H , and the heat transfer coefficient α . Mathematical treatment of the experimental results within the similitude theory yielded the following expression for determining the dimensionless ignition delay time:

$$\tau_3 = 0.016 \theta^2 H^{-m},$$

where

$$\theta_n = \frac{E}{RT_0^2} (T_0 - T_n); \quad H = a \left[\frac{RT_0^2}{E} \frac{1}{Qk_0\lambda} \exp(E/RT_0) \right]^{1/2}; \quad \gamma = \frac{C_p}{Q} \frac{RT_0^2}{E}.$$

Here, Q is the thermal effect; C , specific heat; E , activation energy; and $m = 1.64$. A graphical presentation of the experimental results in dimensionless coordinates shows that only under the following conditions $\tau_3(\infty) \ll \tau_3(H) \ll \tau_3(0)$, does the above equation correctly describe the ignition of pyroxylin by hot gases and is probably applicable for other condensed systems in which the ignition is not accompanied by phase transitions.

33. Maksimov, E. I., A. G. Merzhanov, and N. N. Semenov. A model of the combustion of nonvolatile explosives. IN: Akademiya nauk SSSR. Doklady, v. 157, no. 2, 1964, 412-415.

Parr and Crawford's theory of burning of liquid explosives through the formation of foam in the condensed reaction zone (J. Phys. Coll. Chem., 54, no. 6, 1950, 927) has been further developed by theoretically treating the problem of the mechanism of dispersion during the burning of nonvolatile liquid and solid explosives. A single-stage model of the burning process is considered which takes into account reactions in the liquid phase with a large expansion in volume caused by the formation of foam, which is transformed into an aerosol. The reaction in the gaseous phase, the dissolution of the gaseous reaction products in the liquid phase, and the heat losses from the reaction zone are ignored. The heat capacity is assumed to be constant. The equation of state for an ideal gas is applied to the pressure in the foam bubbles and the aerosol. An approximate solution of the initial system of equations derived for the burning process with a large expansion in volume was obtained by using Zeldovich and Frank-Kamenskiy's

assumption that the convective heat transfer in the reaction zone may be neglected. Numerical values of various parameters of the burning process were calculated on an electronic computer to verify the approximation. The data were in fair agreement with the theory. Thus, the proposed model may be used for calculating the burning velocities of liquid and melting, solid explosives.

34. Maksimov, E. I., A. G. Merzhanov, and V. M. Shkiro. Gasless compositions as the simplest combustion model for nonvolatile condensed systems. *Fizika gorennya i vzryva*, no. 4, 1965, 24-30.

Condensed phase reactions are of fundamental importance for studying solid propellant combustion. However, the presence of gasification processes and gas-phase reactions affects the combustion mechanism so that the characteristics of the condensed-phase reactions can be studied only with a model mixture in which no gases are formed. Most of the known thermites have been found to be unsuitable for this purpose, since they all exhibit a considerable pressure effect on the burning velocity, thus indicating the presence of gas-phase reactions. Therefore, to formulate a thermite which would react only in the condensed phase, a mixture of 25% Al and 75% Fe_2O_3 was diluted with various amounts of Al_2O_3 so that the burning temperature was lowered below the boiling temperatures of any of its components or products. These mixtures were compacted to densities in the range of $0.1 < \rho/\rho_{\text{max}} < 0.7$ ($\rho_{\text{max}} = 4 \text{ g/cm}^3$). Tests showed that the burning velocity was fully independent of pressure as predicted. The maximum burning temperature

vs the burning velocity curve was linear, but at about 2600°K, it had a break which is attributed to the onset of the boiling of aluminum. The burning velocity vs density curve had a characteristic minimum. This is attributed to the effect of the thermal diffusivity, since the burning velocity vs the thermal diffusivity curve had the same characteristic. The burning velocity was independent of particle size which indicates that the process is not diffusion controlled, but rather it occurs in a purely kinetic regime. The burning velocity can therefore be described by the following formula derived from the thermal combustion theory:

$$u_{21}^2 = a \frac{c}{Q(1-\eta)} \cdot \frac{RT_m^2}{E} K_0 \exp\left(-\frac{E}{RT_m}\right),$$

where a is the thermal diffusivity; R , gas constant; K_0 , pre-exponential factor; E , activation energy; Q , thermal effect of the reaction of a stoichiometric mixture in the liquid state; c , mean heat capacity; and η is the dilution factor. The experimental results were in good agreement with values calculated by this formula. Therefore, it can be used for calculating the

kinetic parameters E and K_0 , which were calculated to be 130 kcal/mole and 10^{15} l/sec, respectively, for the mixture tested. It is concluded that the tested model mixture can be used for further studies of complex combustion processes which also involve gas phase reactions.

35. Maksimov, E. I., A. G. Merzhanov, and V. M. Shkiro. Self-ignition of thermite mixtures. Zhurnal fizicheskoy khimii, v. 40, no. 2, 1966, 468-470.

The previously described method for studying thermal explosions (A. G. Merzhanov, V. G. Abramov, F. I. Dubovitskiy, Dokl. AN SSSR, 128, 1238, 1959; V. V. Barzykin, A. G. Merzhanov, Zh. fiz. khim. 38, 2640, 1964) was modified and used for investigating the reaction kinetics and self-ignition temperature of a thermite mixture consisting of Fe_2O_3 52.5, Al 17.5, and Al_2O_3 30%. The mixture was compressed to form cylindrical specimens with a constant length to diameter ratio $l/d = 0.2$, a density $\rho \approx 2.3 \text{ g/cm}^3$, and a thickness varying from 0.095 to 0.320 cm. The specimen was immersed in molten Pb and heated in an electric furnace. The temperature at which a "surf" appeared on the lead surface was found to be the critical self-ignition temperature of the thermite specimen. The critical temperature decreased as the thickness of the specimen increased from 810°C for a 0.095 cm thick specimen to 676°C for a 0.320 cm thick specimen. The activation energy and the rate of the heat of reaction

were calculated to be 40,000 cal/mol and $4.5 \times 10^8 \text{ cal/g-sec}$, respectively. Since there is no gas evolution during a thermite reaction, thermite mixtures may be used as simple models for studying thermal explosions and the self-ignition of condensed systems.

36. Maksimov, E. I., A. G. Merzhanov, and Yu. R. Kolesov.
Density distribution in the combustion zone of condensed systems. IN: Akademiya nauk SSSR. Doklady, v. 162, no. 5, 1965, 1115-1118.

An experimental method based on x-ray absorption measurements was developed for determining the density profile at the burning surface of a solid propellant. The method applied to hexogen combustion at 0.5—5 atm showed that the density profile changes considerably with pressure and that the density change is gradual. The thickness of the zone in which the density changes can be calculated as a function of the propellant density by means of a derived formula. Motion picture photography showed that foam formed in the molten propellant layer leads to aerosol formation. Foam formation is attributed to the chemical reaction in the liquid melt rather than to passage of gases or to boiling of the overheated melt. The chemical conversion in the liquid phase was evaluated as 0.15—0.35. A comparison of the velocity of the reaction front propagation with the burning velocity actually observed showed that the former is one order of magnitude smaller than the latter and that the gas phase reaction

must thus be the controlling step in the overall combustion process. The study reconfirmed a previous theoretical result that the density changes gradually and not stepwise. Values of the surface temperature, which are the basis for many combustion theories, should therefore be considered with reservations.

37. Mal'tsev, V. M., and P. F. Pokhil. Evaluation of the thermal effect in the initial combustion stage of explosives. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 2, 1963, 173-174.

The effect of the condensed phase reaction taking place during combustion of explosives was studied. The heat evolved during the condensed phase reaction Q_1 was calculated at different pressures by the formula $Q_1 = Q_3 - Q_2$, where Q_2 equals the amount of heat transferred from the smoke-gas zone to the explosive and Q_3 equals the total heat transferred to the explosive during combustion. The values of Q_2 and Q_3 were experimentally determined by measuring the surface temperature of the explosive and determining the axial temperature profile in the flame. Measurements with nitroglycerine were made at 22 to 66 atm; Q_1 , Q_2 , Q_3 , Q_4 (heat evolved in the gas phase), and Q (total reaction heat) were tabulated. The table shows that Q_1 increases with increasing pressures, while the amount of smoke generated by dispersion of the condensed phase decreases. Measurements of the absorption and temperature profiles of the flame were also made with hexogen and the results plotted for 20, 40, and 60 atm. The

plot shows that two different flame zones exist: 1) a zone close to the surface in which absorption decreases rapidly with increasing distance from the surface; this is explained by the fact that the concentration of the dispersed aerosol particles is highest at the surface and decreases rapidly with distance from the surface owing to evaporation; and 2) a zone in which absorption approaches a minimum value with increasing distance from the surface. Absorption in the second zone increases with increasing pressure, and as the pressure increases, the temperature profile becomes steeper and the maximum flame temperature is shifted toward the surface. The results for hexogen show that about 15 kcal/g (about 10% of the total heat transferred to the explosive) is evolved in the condensed phase. At medium and high pressures, the initial stage in the combustion of hexogen takes place in the condensed phase. Consequently, the heating of hexogen during combustion takes place by heat conduction from the gas phase as well as by heat evolution in the condensed phase.

38. Mal'tsev, V. M., V. S. Logachev, and V. A. Seleznev. Accounting for some optical properties of ballistic powder flames in temperature measurements. Zhurnal fizicheskoy khimii, v. 38, no. 11, 1964, 2666-2668.

The optical temperature measurement of the flame of ballistic powder was studied in a constant pressure bomb by determining the emission spectrum (3800 to 7000 Å), the brightness temperature, and the reflectivity and absorptivity of the flame. It is concluded that optical methods may be used for temperature measurements of powder flames at elevated pressure.

39. Maneliš, G. B., and Yu. I. Rubtsov. The kinetics of thermal decomposition of ammonium perchlorate. Zhurnal fizicheskoy khimii, v. 40, no. 4, 1966, 770-774.

The kinetics of thermal decomposition of ammonium perchlorate AP were studied in the 196.5—280°C range. The kinetic constants and the heat of the reaction were determined. Examination of the kinetic curves obtained by gravimetric methods indicates that in the 200—280°C range, the reaction rate drops sharply after 30—35% of the starting sample decomposes; the reaction continues at a relatively low rate. It was also observed that above 236°C, AP changes from an orthorhombic to a cubic crystalline modification. The transition is accompanied by a substantial decrease in the reaction rate, since in the cubic crystal lattice the decomposition develops more slowly. The heat of reaction was found to be 348 ± 11 cal/g in glass vessels, and 334 ± 12 cal/g in aluminum vessels. Mass-spectrometric analysis of the decomposition products showed that, in addition to nitrogen oxides, appreciable amounts of free nitrogen are present.

40. Margolin, A. D., and S. V. Chuyko. Conditions of ignition of pore walls in the combustion of porous charges. Fizika gorennya i vzryva, no. 3, 1965, 27-35.

Several investigators have previously concluded that instability is connected with the ignition of pore walls, but the conditions have not been analyzed. The ignition or pyrolysis of pore walls is considered to be a necessary but not a sufficient condition for combustion instability. For instability to occur, the front of the ignition or pyrolysis must move faster than the normal combustion front. Perturbation of the normal combustion regime can take place either by penetration of gases into the pores or by heating the gases contained in the pores. In the present study, ignition criteria were derived in terms of pore dimensions, gas and propellant temperatures, pressure, etc. The following cases were mathematically analyzed: heating and ignition of pores by penetrating hot gases, ignition of the pore wall caused by flame propagation into the gases contained in the pores, and heating of gases by adiabatic compression. The effects of imperfections in pore structure are also discussed.

41. Margolin, A. D. Interaction of the combustion zones and the anomalous pressure dependence of the burning velocity. Zhurnal fizicheskoy khimii, v. 38, no. 6, 1964, 1599-1601.

A theoretical analysis has been made of the effect of the interaction between burning zones in a system on the burning velocity of the system. A simple two-zone theoretical model is proposed for the interaction between the first zone (reactions in the condensed phase) and the second zone (reactions in the adjoining gaseous phase). The model explains the anomalous pressure dependence of the burning velocity of a system. The pressure dependence of the burning velocity of the entire system is characterized by the function v :

$$v = \frac{a_2 v_1 - a_1 v_2}{a_2 - a_1},$$

where $a_1 = (d \ln u_1 / d \ln y)_{y_0}$; $a_2 = (d \ln u_2 / d \ln y)_{y_0}$; $v_1 = (d \ln u_1 / d \ln p)_y$; $v_2 = (d \ln u_2 / d \ln p)_y$; y_0 and y refer to the distances between the zones, and u_1 and u_2 refer to the burning velocities in the two zones.

According to this theory, the anomalous pressure dependence of the burning velocity is explained as follows: at low pressures the gas-phase reaction is a controlling factor with $v = v_2^0 = (d \ln u_2 / d \ln p)_T$; the reaction then follows the region of strong interaction between the zones at low v ($v < v_1$; $v < v_2$); as the pressure increases, the condensed phase reaction becomes the controlling factor and $v = v_1^0 = (d \ln u_1 / d \ln p)_T$. The equation may also be used for studying other parameters if p (pressure) is replaced by a different parameter such as particle size or additive concentration. The equation may be generalized to include the interaction of more than two zones.

42. Margolin, A. D., O. I. Nefedova, and P. F. Pokhil.
Dependence of burning rate of various fuels on the initial temperature. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 3, 1964, 149-153.

Experiments were made with hexogen and mixtures of potassium perchlorate with tungsten, zirconium, or potassium benzoate. Initial temperatures ranged from -140 to 150°C. The component ratios, charge densities, and inert-gas pressure were varied in the experiments. The log of the burning rate of hexogen and mixtures of potassium perchlorate with metals was found to have a linear dependence on the initial temperature of the substance, but the relation for mixtures of potassium perchlorate with potassium benzoate has a break in it. Measurements of the surface temperatures in flameless combustion showed that the heat released in the reaction layer of the condensed phase, on raising the initial temperature of the pyroxyline powder from 90 to 140°C, decreases 15% (from 84 to 72 cal/g). The heat capacity of the products that form the smoke-gas mixture and the powder is computed to be 0.4 cal/g deg.

43. Merzhanov, A. G., and A. K. Filonenko. Theory of reaction regimes in flames in the combustion of nonvolatile condensed systems. IN: Akademiya nauk SSSR. Izvestiya. Seriya khimicheskaya, no. 8, 1964, 1509-1511.

The length of the dark preflame zone x_m and the mass burning rate u_m were determined by combustion of pyroxiline samples (1 cm in diameter, 3-4 cm long) which were compressed to densities ranging from 0.8 to 1.5 g/cm³. The experiments were conducted at 20-30 atm pressure in a constant pressure bomb filled with nitrogen. The results (see Figs. 1 and 2) showed that the experimental data can be correlated by the previously derived theoretical relationship:

$$x_m = u_m F(T_0) / p Q(p),$$

where $F(T_0)$ is a known temperature function at the beginning of the plateau in the flame temperature profile, $Q(p)$ is the thermal effect of the reaction in the gas phase, and p is the pressure.

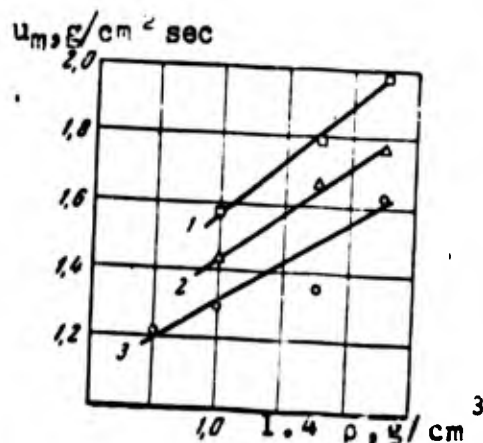


Fig. 1. Dependence of the mass burning rate of pyroxiline on density at different pressures

1 - 30 atm; 2 - 26 atm;
3 - 21 atm.

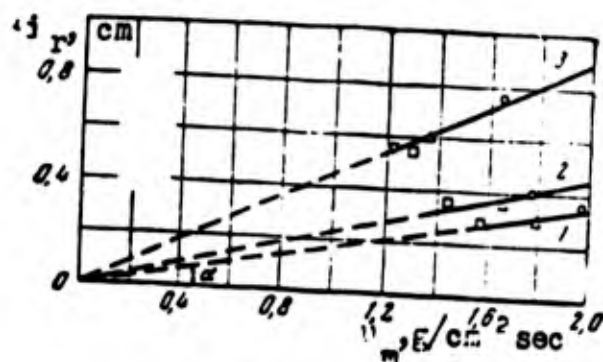


Fig. 2. Dependence of the length of the dark zone on the mass burning rate at different pressures

1 - 31 atm; 2 - 26 atm; 3 - 21 atm; ∇ - $\rho = 0.8$; $\square$ - $\rho = 1.0$; Δ - $\rho = 1.3$; $\circ$ - $\rho = 1.5$.

44. Novikov, S. S., and Yu. S. Ryazantsev. Acoustic admittance of the hot surface of condensed systems. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 6, 1964, 77-80.

On the basis of a theory of Ya. B. Zel'dovich, an expression is derived for the acoustic admittance of the hot surface of a condensed system which is dependent on three parameters. It is shown that, depending on these parameters, acoustic waves reflected from the hot surface may be intensified or attenuated. Acoustic waves having a wavelength considerably greater than the width of the burning zone in the gas are considered, so that, in the given case, the front of the chemical reaction in the gas coincides with the surface of the condensed phase. To determine the acoustic admittance of the hot surface, it is necessary to determine the ratio of the magnitudes of the velocity and pressure of the sound field on this surface.

45. Novikov, S. S., and Yu. S. Ryazantsev. Analysis of mathematical models of combustion in the condensed phase. IN: Akademiya nauk SSSR. Doklady, v. 157, no. 5, 1964, 1188-1191.

The combustion of condensed systems is characterized by the multistage conversion of the combustible in the combustion front. Therefore, the study of the individual stages and their interaction and the determination of the controlling stage are of importance. It was previously shown that up to 70% of the heat required for heating the burning surface is liberated by chemical reactions in the condensed phase. In flameless combustion of nitroglycerine powder, combustion is sustained exclusively by heat liberated in the condensed phase. It was also previously found that with increasing pressure, the heat liberated in the condensed phase increases. In the present article, the existence and uniqueness of the solution of the equations describing the combustion process in the condensed phase was proven. Ya. B. Zel'dovich's thermal theory of combustion in gases was generalized for the case of combustion in the condensed phase. Two models were considered: 1) the T_s -model, where T_s is a fixed temperature analogous

to the boiling point in the Zel'dovich-Belyayev model; and 2) the Q_k model, in which the condensed phase is gasified when a fixed amount of heat (Q_k) is evolved by chemical reaction in the condensed phase. The uniqueness of both solutions was proved. It was also shown that both models are not mutually exclusive and can be used simultaneously. For this case the possibility of a "subsurface" combustion regime as a function of pressure is discussed.

46. Novikov, S. S., and Yu. S. Ryazantsev. Combustion theory of condensed systems. IN: Akademiya nauk SSSR. Doklady, v. 157, no. 6, 1964, 1448-1450.

The problem of the existence of a single solution of equations of condensed phase combustion is investigated on the assumption that the reaction in the condensed phase is monomolecular and the effect of the gaseous phase manifests itself by the presence of a heat flow from the gaseous to the condensed phase.

47. Novikov, S. S., and Yu. S. Ryazantsev. Interaction of sound waves with the burning surface of condensed systems. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 2, 1966, 57-62.

The problem of the acoustic admittance of burning surfaces of condensed explosives and the effect of reflected sound waves on the combustion stability were studied theoretically. The exothermic reaction in the condensed phase, its effect on the burning velocity, and the change in the condensed-phase surface temperature under nonsteady-state conditions were taken into account. A theoretical model of the combustion process was used in which the burning zone consisted of five regions: 1) a heating region in the condensed phase without a chemical reaction; 2) a chemical reaction region in the condensed phase; 3) a heating region of the gas phase also without a chemical reaction; 4) a chemical reaction region in the gas phase; and 5) a region with gaseous combustion products. Equations describing the linear perturbation of the combustion parameters in regions 1-4 at a harmonic pressure change were derived. Acoustic properties of the burning surface of the condensed phase are characterized

by the acoustic admittance of the burning surface, for which an equation was also derived. The conditions under which sound wave amplification takes place are given. Values of several dimensionless parameters were calculated and plotted. A comparison of the calculated data with corresponding published experimental data for ballistic powders showed good agreement for high-pressure combustion. There is a marked disagreement between the experimental and theoretical data obtained for low-pressures.

48. Novikov, S. S., and Yu. S. Ryazantsev. Theory of combustion stability of solid propellants. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 1, 1965, 57-61.

Mathematical criteria of the combustion stability of solid propellants were derived for the zero- and 1st-order reactions in Q-model combustion, when the gasification of the condensed phase (k-phase) occurs as a result of the exothermic reaction in the k-phase, and for the zero- and 1st-order reactions in T_s -model combustion, when the gasification of the k-phase occurs as a result of the surface, gaseous-phase temperature T_s . The proposed combustion stability theory takes into account the heat generated in the k-phase. The effect of the heat generated in the surface layer of the k-phase and the temperature fluctuations in the gaseous phase near the charge surface on the combustion stability of solid propellants is discussed.

49. Novikov, S. S., and Yu. S. Ryazantsev. The theory of the steady propagation velocity of an exothermic reaction front in the condensed phase. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 3, 1965, 43-48.

The exothermic reaction in the condensed phase may in some cases liberate up to 80% of the total heat release in the combustion of a solid propellant. However, even in cases when the heat release in the condensed phase is much smaller, this process is fully or partly responsible for the gasification and thus has a controlling effect on the overall combustion process. Formulas for the velocity of the reaction front propagating in the condensed phase are also of importance for analyzing nonsteady-state phenomena associated with combustion instability. In the present study, the Zel'dovich-Frank-Kamenetskiy method for thermal flame propagation was applied, and formulas were derived for calculating the velocity of the reaction front propagating due to a first- or zero-order reaction in the condensed phase. Formulas for the maximum and minimum velocities were also obtained.

50. Novozhilov, B. V. Powder combustion during harmonic pressure changes. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 6, 1965, 141-144.

A theoretical analysis of solid propellant combustion showed that a solid propellant constitutes an oscillating system with a natural frequency and a damping decrement. The model was based on the assumption that the surface temperature T_s depends on the pressure p and the initial temperature T_0 . The relationship for the steady-state burning velocity $m(T_0, p)$ was then transformed to the relationship for the nonsteady-state burning velocity $m(f, p)$, where f is the temperature gradient at the surface. Relationships in terms of k , r , and m , where

$$k = (T_s^0 - T_0) \left(\frac{\partial \ln m^0}{\partial T_0} \right)_p, \quad r = \left(\frac{\partial T_s^0}{\partial p} \right)_p$$

$$v = \left(\frac{\partial \ln m^0}{\partial \ln p} \right)_{T_0}, \quad \mu = \frac{1}{T_s^0 - T_0} \left(\frac{\partial T_s^0}{\partial \ln p} \right)_{T_0}$$

were derived. It was shown that a stable regime characterized by $k > 1$ and $r \geq (k-1)^2/(k+1)$ can be re-established by relaxation of the nonsteady-state tem-

perature distribution. The time exponent characterizing the approach to the steady-state regime has the form $\exp[\Omega(u^0)^2 \cdot t/\kappa]$, where $u^0 = m^0/\rho$ (burning velocity), and

$$\Omega = \frac{(k-1)^2 - r(k+1)}{2r^2} \pm i \frac{k-1}{2r^2} \sqrt{(2k-r+2)r - (k-1)^2}.$$

$\lambda = -\text{Re}\Omega$ is the decrement which characterizes damping of the oscillations.

$$\text{Im}\Omega = \pm \sqrt{k^2 - r^2}$$

characterizes the oscillation frequency. The character of the oscillating regime depends on the ratio λ/ω . When $\lambda \ll \omega$, the damping is small. As r approaches $(k-1)^2/(k+1)$, i.e., at the stability limit, λ approaches 0. Thus, it can be seen that when $k > 1$, the propellant is an oscillating system with a given frequency and damping decrement. When $k < 1$, the steady-state regime is approached aperiodically, i.e., without passing through the steady-state value. Expressions for the burning velocity in the presence of forced harmonic oscillations were also derived and conditions for resonance were analyzed. It was shown that the

equations and boundary conditions characterizing resonance are nonlinear, so that all phenomena related to nonlinear oscillations such as ambiguous relationships between the burning velocity and the pressure fluctuation frequency, sudden transitions between regimes, and resonance at frequencies not coinciding with the natural frequency can be expected.

51. Novozhilov, B. V. Stability criterion for steady-state powder combustion. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 4, 1965, 157-160.

An analysis of solid propellant combustion was made on the basis of a model which was assumed to have a variable propellant surface temperature and a two-stage combustion process during which the propellant is first decomposed and gasified and then reacts in the gas phase to yield the final products (see Fig. 1). It is assumed that the reactions in the gas and condensed phases take place without inertia. The heat release due to decomposition of the condensed and dispersed phases and that of the gas-phase reaction are considered. Based on the concept that combustion is either stable or unstable when small perturbations of the burning velocity or surface temperature are either damped or amplified, the following stability criteria were derived. Combustion is always stable when $k < 1$; when $k > 1$, it is stable only when

$$r > \frac{(k-1)^2}{k+1} ;$$

where,

$$k = (T_1 - T_0) \left(\frac{\partial \ln m}{\partial T_0} \right)_p$$

and

$$r = (\partial T_1 / \partial T_0)_p$$

Here, m is the mass burning rate; ϕ , temperature profile; T_1 , surface temperature; and T_0 , initial propellant temperature. It is noted that for steady-state stability analysis only $m(\phi, p)$ must be known, while under nonsteady-state conditions also $T_1(\phi, p)$ must be known.

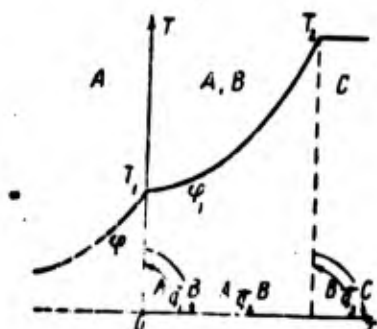


Fig. 1. Solid propellant combustion model

A → B → C - Two-stage conversion;
 q_1 - heat released by decomposition on surface;
 q_2 - heat released by decomposition of dispersed particles;
 q_3 - heat released by gas-phase reaction;
 T_2 - combustion temperature.

52. Novozhilov, B. V. Temperature dependence of the kinetic characteristics of exothermic reactions in the condensed phase. IN: Akademiya nauk SSSR. Doklady, v. 154, no. 3, 1964, 690-691.

Kinetic studies of explosives undergoing thermal decomposition indicate a large value for the collision number Z , which cannot be correlated with the frequency of molecular collision. The magnitude of Z and also of E (the activation energy) can be explained by the presence of a thermal bond, whose length increases with the temperature. A mathematical expression was derived for the temperature dependence of this thermal bond.

53. Novozhilov, B. V. The mean burning velocity during harmonic pressure changes. Fizika gorennya i vzryva, no. 3, 1965, 41-44.

During slow pressure variations, the temperature profile of a propellant follows the pressure change and the burning velocity has a quasi-steady-state value. When the pressure changes rapidly, the temperature profile lags behind the pressure change and the burning velocity assumes a nonsteady-state value. Novozhilov (PMTF, 1962, 5) and Istratov, Librovich, and Novozhilov (PMTF, 1964, 3) investigated the latter regime by analyzing the effect of instantaneous or exponential pressure changes or changes caused by a sudden nozzle constriction in a solid propellant motor. In the present study, a model is considered in which the burning velocity of the propellant is a function of the pressure and the temperature gradients on the solid surface only. Expressions were derived for evaluating the deviation of the pressure from the steady-state value during harmonic pressure fluctuations. This problem may be important for studying the generation of acoustic oscillations in solid propellant combustion. The analysis showed that for exponential and linear pres-

sure changes, the mean burning velocity in a nonsteady-state regime is lower than the steady-state value at the mean pressure.

54. Pokhil, P. F., and L. D. Romodanova. Investigation of the structure of the surface of burning model mixtures of solid fuels. Zhurnal fizicheskoy khimii, v. 39, no. 2, 1965, 294-299.

To study the mechanism of the combustion of solids, charges of stoichiometric mixtures of oxidants (ammonium perchlorate, potassium perchlorate, and sodium perchlorate) with combustibles (graphite, tungsten, naphthalene, starch, and succinic and malonic acids) were ignited and burned for various periods of time under various conditions, e.g., in vacuo, under pressure, and in air. They were then extinguished, and their surfaces were investigated under a microscope. Analysis of the tabulated results showed that, with the exception of the ammonium perchlorate-tungsten mixture, none of the mixtures with ammonium perchlorate burn steadily at room temperature in vacuo (10^{-2} mm Hg). The burning ceases when the igniting wire is removed from the charge surface. During the application of the hot wire, the combustible materials (except W) melt, and ammonium perchlorate crystals appear on the charge surface. At pressures above atmospheric, the amount of ammonium perchlorate crystals on the burning

surface decreases, and at pressures above 30 atm, the crystals are replaced by holes, which is attributed to the burning of ammonium perchlorate itself at pressures above 30 atm. Depending on the melting or sublimation temperature, either the oxidant or the combustible accumulates on the burning surface. The appearance of small bubbles in the molten layer of the burning mixture indicates a liquid-phase oxidation process. The limiting pressure at which the mixtures containing ammonium perchlorate cease to burn depends on the particle size of the oxidant and on the physical properties of the combustible. Stable combustion was observed for $KClO_4$ -W mixtures at temperatures exceeding $5^\circ C$ and pressures of about 10^{-2} mm Hg. The NH_4ClO_4 -W mixture also burned steadily at room temperature and pressures of 5 atm or more. Mixtures of these oxidants with graphite do not burn steadily in the pressure region studied (up to 100 atm). The initial stage of the burning of solids occurs in the molten layer of the charge, and a high-temperature gaseous phase is formed where the burning is completed.

55. Pokhil, P. F., and L. D. Romodanova. The combustion of systems containing potassium perchlorate as oxidizer and metal fuels in a vacuum. Zhurnal fizicheskoy khimii, v. 39, no. 11, 1965, 2757-2759.

Previous studies by the authors showed that composite propellants containing potassium perchlorate and a metal as a fuel can undergo flameless combustion at 10^{-2} mm Hg pressure. Since the combustion stability of such propellants depends on the condensed phase reaction and the overall heat release, a study was made of the ignition temperatures, the surface temperatures during combustion, the burning velocities, and the chemical composition of the condensed- and gas-phases of propellants containing $KClO_4$ and Mo, Zr, W, or Ti with particle sizes ranging from 20 to 60 μ . The ignition temperatures ranged from 370°C for $KClO_4 + Mo$ to 610°C for $KClO_4 + Ti$, while the surface temperatures of these propellants were 610 and 640°C, respectively. This indicates that after ignition, the surface temperature increases due to the exothermal reaction in the condensed phase. Chemical analysis of the condensed and gas phases during combustion of

$KClO_4 + Zr$ showed that only 7% of oxide is formed, but 30% $KClO_4$ decomposes in the condensed phase. This shows that in the initial combustion stage, the reaction takes place only on the metal surface; then a gas-smoke phase is formed in which combustion is completed. Another important conclusion is that ignition takes place at a temperature at which the metal is in a solid state.

56. Pokhil, P. F., and V. M. Mal'tsev. On the mechanism of gunpowder combustion. *Inzhenerno-fizicheskiy zhurnal*, v. 6, no. 6, 1963, 94-99.

The distribution of light absorption and temperature along the axis of a flame of nitroglycerine powder (Balistite H) and hexogen at pressures of $(220.5 \text{ to } 440.1) \cdot 10^4 \text{ newton/m}^2$ was measured in a constant-pressure bomb by an infrared pyrometer originally developed for temperature measurements at $600\text{--}3500^\circ\text{K}$. Three distinct zones were observed on the curves of temperature and absorption vs distance. Absorption decreased to a minimum in the first zone and increased in the second. In the third zone the temperature reached a maximum. Only two zones were observed for hexogen; absorption decreased in the first zone and remained constant in the second. The results indicate that the condensed phase decreased during combustion of the powder and the combustion efficiency and temperature increased continuously with pressure up to a maximum of 2350°K at $(490\text{--}539) \cdot 10^4 \text{ n/m}^2$. The length of the combustion zone decreased with increasing pressure. The temperature profile of the powder flame was S-shaped. Determination of the heat release showed that in the

condensed phase it increased with increasing pressure. The amount of heat released in the condensed phase and its role in heating charges, compared to the overall heat release, were greater for nitroglycerine powder than for hexogen.

57. Pokhil, P. F., and V. M. Mal'tsev. Combustion temperature of explosives. Zhurnal fizicheskoy khimii, v. 39, no. 4, 1965, 978-979.

The combustion temperatures of PETN, hexogen, and tetryl were measured at high pressures (20—100 atm) in a constant-pressure bomb in a nitrogen atmosphere. A previously described experimental unit was used (P. F. Pokhil, V. M. Mal'tsev, and L. I. Gal'perin, Zh. fiz. khimii, v. 34, 1131, 1960). The flame absorptivities of PETN and hexogen were in the 0.1—0.3 range and that of tetryl in the 0.8—0.9 range. In all cases, the absorptivity increased along the flame height towards the charge surface. The temperature of the flames of PETN and hexogen in the pressure range of 20—60 atm increased rapidly; in the pressure range of 60—100 atm, the temperature rose slowly to a maximum of 3250 and 3150°K, respectively. In this pressure range (20—100 atm), the tetryl flame temperature changed only slightly and was 2600°K. In all cases, the measured temperatures were lower than calculated. At high pressures, the explosives were partially dispersed at the surface of the liquid layer of the charges.

58. Shaulov, Yu. Kh., G. O. Shmyreva, and V. S. Tubyanskaya. Heat of combustion of ammonium borane. Zhurnal fizicheskoy khimii, v. 40, no. 1, 1966, 122-124.

The heat of combustion at a constant volume ΔU of ammonium borane BH_3NH_3 was determined experimentally and its standard heat of formation ΔH_F^0 was calculated. The exact value of ΔH_F^0 is necessary for solving problems connected with the synthesis of BH_3NH_3 . ΔH_F^0 was calculated from the equation: $\Delta H_F^0(\text{BH}_3\text{NH}_3(\text{cr})) = \Delta H_F^0(\text{H}_3\text{BO}_3(\text{cr})) + 1.5 \Delta H_F^0(\text{H}_2\text{O}(\text{liq})) - \Delta H_C^0(\text{BH}_3\text{NH}_3(\text{cr}))$, where $\Delta H_F^0(\text{H}_3\text{BO}_3(\text{cr}))$ and $\Delta H_F^0(\text{H}_2\text{O}(\text{liq}))$ are taken from previously published data and $\Delta H_C^0(\text{BH}_3\text{NH}_3(\text{cr}))$ is the standard heat of combustion of BH_3NH_3 , which was calculated from the experimental ΔU . ΔU was determined calorimetrically by burning powdered BH_3NH_3 in oxygen under 30 atm at an initial temperature of $25 \pm 0.001^\circ\text{C}$. The calorimetric procedure and analysis of combustion products (boric acid and nitrogen) were described. Combustion of powdered BH_3NH_3 was 99.5—100% complete and scattering of data was 0.2%. The average $\Delta H_C^0(\text{BH}_3\text{NH}_3(\text{cr}))$ was -322.4 ± 0.7 kcal/mol and the calculated $\Delta H_F^0(\text{BH}_3\text{NH}_3(\text{cr}))$ was -42.54 ± 1.4 kcal/mol.

59. Shidlovskiy, A. A., and N. A. Volodina. Study of the combustion of potassium chlorate-identol mixtures with catalytic additives. Zhurnal prikladnoy khimii, v. 39, no. 4, 1966, 754-758.

The burning velocities and combustion temperatures of KClO_3 -phenol formaldehyde resin mixtures containing MnO_2 , KMnO_4 , Cr_2O_3 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Co_2O_3 , and CoO as additives were determined. The burning velocity vs resin concentration curves showed that the burning velocity and combustion temperature are maximum at a resin concentration of 14-18%. The addition of Cr_2O_3 , MnO_2 , and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ had the strongest catalytic effect among the additives tested. They considerably increased the burning velocity and permitted a low caloric mixture containing only 0.8-4% resin to burn at atmospheric pressure. The strongest catalytic effect was experienced when the additives were present in concentrations ranging from 3 to 5%. A stoichiometric mixture of NaClO_3 -resin burned considerably slower than a stoichiometric KClO_3 -resin mixture. This is attributed to the lower melting point of NaClO_3 .

60. Shidlovskiy, A. A., L. F. Shmagin, and V. V. Bulanova. Combustion of ammonium perchlorate under atmospheric pressure. IN: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, v. 7, no. 5, 1964, 862-863.

The catalytic effect of Cu_2O , Cu_2Cl_2 , CuO , CuCO_3 , MnO_2 , MnCO_3 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, Co_2O_3 , ZnO , Fe_2O_3 , NiO , Ni_2O_3 , Cr_2O_3 , Cu , Cr_2O_4 , CdO , or MgO on the thermal decomposition and burning of ammonium perchlorate was studied at atmospheric pressure. The experiments were conducted with technical-grade NH_4ClO_4 sifted through a no. 61 sieve and containing 5% of the pure ground catalysts. The mixtures were burned at 20 and 100°C in glass tubes. At 20°C, NH_4ClO_4 burns in the presence of Cu_2O , CuO , Cu_2Cl_2 , MnO_2 , or MnCO_3 , and at 100°C in the presence of CuCO_3 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, Co_2O_3 , or ZnO . The highest burning velocity and highest thermal coefficient of the burning velocity (0.60-0.80 mm/sec at 20°C and 1.40 to 2.08 mm/sec at 100°C) are exhibited by mixtures containing copper compounds. Mixtures with Fe_2O_3 , NiO , Ni_2O_3 , Cr_2O_3 , Cu , Cr_2O_4 , CdO , and MgO do not burn under the above conditions.

61. Shidlovskiy, A. A., L. F. Shmagin, and V. V. Bulanova.
The effect of some additives on the thermal decomposition of ammonium perchlorate. IN: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, v. 8, no. 4, 1965, 533-538.

The purpose of this work was to investigate the thermal decomposition of ammonium perchlorate AP in the presence of oxides, chlorides, carbonates, and oxalates of certain metals. The decomposition was studied gravimetrically, at atmospheric pressure, and at 214—470°C. The following values for activation energies were found: for the orthorhombic form, $E = 40$ kcal/mole; for the cubic form, $E = 24—28$ kcal/mole; for the residue from the low-temperature decomposition, $E = 36—39$ kcal/mole. Compounds of manganese and cobalt promote complete decomposition of AP at $T < 240^\circ\text{C}$. Compounds of iron, nickel, and chromium promote complete decomposition of AP at 270—280°C. The rate of decomposition of AP is increased by the addition of compounds of copper, manganese, cobalt, as well as zinc oxide; it is retarded by the addition of compounds of iron, bivalent nickel, chromium, and vanadium pentoxide.

For the same element, the activity of the compounds added decreases in the following order: carbonate (oxalate), oxide, and chloride.

62. Shidlovskiy, A. A. Thermochemical estimate of the ability of inorganic ammonium and hydrazinium salts to sustain combustion and explosion. Zhurnal fizicheskoy khimii, v. 39, no. 9, 1965, 2163-2168.

A method was developed for estimating the exothermal effect of the decomposition of ammonium salts whose heats of formation are not known. It is pointed out that ammonium salts which decompose exothermally can, under certain conditions, sustain and propagate combustion and explosion. The ability of ammonium salts to sustain combustion and explosions was studied on the basis of the standard heats of formation of several acids. A constant difference of 27.5 ± 1 kcal/mole between the heats of formation of corresponding ammonium and hydrazinium salts of monobasic acids was determined. The heats of formation of dihydrazinium sulfate and dihydrazinium sulfite were determined; both compounds should be able to sustain combustion. The possibility of exothermal decomposition of hydrazinium tellurate, selenite, and to a lesser extent, of hydrazinium carbonate is suggested.

63. Shteynberg, A. S., V. B. Ulybin, V. V. Barzykin, and A. G. Merzhanov. Ignition of condensed substances at a constant surface temperature. Inzhenerno-fizicheskii zhurnal, v. 10, no. 4, 1966, 482-486.

To verify the previously postulated theory of the ignition of condensed explosives (Averson, A. E., Barzykin, V. V., Merzhanov, A. G. IFZh, 9, no. 2, 1965), the ignition of pyroxylin No. 1 charges having a constant initial surface temperature ($T_1 = 255-369^\circ\text{K}$) by contact with an aluminum block with a varying temperature ($T_0 = 485-525^\circ\text{K}$) was studied experimentally using a specially developed experimental unit. The initial temperature of the pyroxylin was set by a thermostat, and the temperature of the igniter was set by a current control system. The ignition delay t_z was visually observed and recorded using a stopwatch. The temperature of the ignition block was varied to obtain an ignition delay of 3-20 sec. The experimental data were treated by an equation derived by mathematical transformation of the published theoretical equation for t_z . The graphed results show satisfactory agreement between the theoretical and the experimental data. The activation energy calculated from the graphs was found to be 200 kJ/mole.

64. Solymosi, Frigyes, and Klara Dobo. The effect of impurities on the thermal decomposition and explosion of ammonium perchlorate. *Magyar kemiai folyoirat*, no. 3, 1966, 124-129.

The thermal decomposition of ammonium perchlorate was studied in the presence of low concentrations (below 1%) of different impurities, such as iodide, bromide, silver (I), copper (II), and iron (III) ions. Detailed kinetic measurements were made between 200 and 240°C as well as 260 and 330°C. In the lower temperature range, all the impurities decrease the induction period and increase the rate of decomposition of ammonium perchlorate. The activation energies found for the catalytic decomposition are in good agreement with the values corresponding to a process occurring via an electron transfer mechanism. At temperatures above 260°C, the decomposition of contaminated ammonium perchlorate became extremely rapid and led to explosion. This indicates that the presence of impurities may lower the explosion temperature by about 140 to 180°C. The effect of the impurities is explained in terms of electron transfer catalysis, and the part played by the character of the impurity is considered.

65. Strunin, V. A., and G. B. Manelis. Effect of pressure on the kinetics of thermal decomposition of ammonium perchlorate. IN: *Akademiya nauk SSSR. Izvestiya. Seriya khimicheskaya*, no. 12, 1964, 2226-2227.

The thermal decomposition of ammonium perchlorate was studied at 230 and 260°C in a nitrogen atmosphere, at atmospheric pressure, and at 100 atm. It was determined that the inert-gas pressure has no effect on the kinetics of thermal decomposition.

66. Strunin, V. A. Condensed combustion zone of explosives. Zhurnal fizicheskoy khimii, v. 39, no. 2, 1965, 433-435.

Previous studies of the condensed phase burning of explosives do not account for the kinetics of the chemical reactions occurring during combustion. An equation which takes into account the kinetics of chemical reactions was derived for calculating the condensed phase burning velocity u of explosives. Expressions correlating other parameters of the burning (temperature T ; degree of conversion η ; degree of dispersion n_d ; activation energy E ; and thermal diffusivity a) of explosives were also derived. To verify the theory, u , η , n_d , and a for the condensed phase burning of mercury fulminate, which burns without flame in vacuo, were calculated using the derived equations. The calculated data are in fair agreement with the experimental data.

67. Sulimov, A. A., and A. I. Korotkov. Effect of the high-temperature zone of the gas phase on the rate of burning of nitroglycerin. Zhurnal fizicheskoy khimii, v. 38, no. 2, 1964, 331-333.

The effect of the temperature of the gas phase on the burning rate u of nitroglycerin and pyroxylin was studied by burning the propellants in a bomb under nitrogen and recording the burning process with motion picture photography. Specimens of nitroglycerin or pyroxylin were cemented to plexiglass plates and placed 10 to 12 mm from each other. The burning was initiated by burning black powder in the gap between the plates. At small distances between the propellant and the maximum temperature zone ($z < 2h_m$, where h_m is the distance between the propellant surface and the maximum temperature zone in the gap), u is lower than the steady-state value. This is attributed to the absence of a gas phase with a complete temperature profile in the gap between the plates.

68. Tsyganov, S. A., N. N. Bakhman, and V. V. Yevdokimov. Combustion of condensed systems with polydispersed components. Fizika gorennya i vzryva, no. 4, 1965, 44-51.

Previous studies have shown that propellants containing polystyrene and NH_4ClO_4 with small size particles (15μ) burn slower than those with larger particle size oxidizers ($300-400 \mu$). This is explained by the fact that in combustion with the small particle oxidizer, the reaction in the interaction zone takes place at an excess of oxidizer. When part of the small size oxidizer is replaced by a larger size oxidizer, the mixture is enriched in fuel and the reaction takes place faster. To study this phenomenon in greater detail, experiments were made with an NH_4ClO_4 -polystyrene mixture at oxidizer/fuel ratios of 1, 0.7, 0.5, and 0.2, with NH_4ClO_4 -plexiglass mixtures at fuel/oxidizer ratios of 2, 1, and 0.7, and with perchlorate-asphalt mixtures. Nongelatinized mixtures and mixtures gelatinized with dichloroethane were used. The experiments were made at 5, 10, 25, 40, 70, and 100 atm. The NH_4ClO_4 had either large particles ($300-400 \mu$), small particles (6μ), or a 50 to

50% mixture of large and small particles. It was found that the propellants with the mixed particle oxidizer can burn at any rate ranging from that of the large particle size to that of the small particle size depending on the fuel/oxidizer ratio. The parameter Y characterizing the burning velocity was defined by the equation:

$$Y = \frac{u_{\text{mix}} - u_{\text{lar}}}{u_{\text{sm}} - u_{\text{lar}}}$$

where u_{mix} , u_{lar} , and u_{sm} are the burning velocities with mixed, large, and small oxidizer particles, respectively. It was found that when Y increases with increasing pressure, the dependence of the burning velocity on the pressure will be more pronounced with the mixed particle oxidizer than with either the small or larger particle oxidizer. However, when Y decreases as the pressure increases, the dependence of the burning velocity on the pressure is less pronounced with the mixed particle oxidizer than with either the large or small particle oxidizer. The fact that the burning velocity becomes less dependent on pressure had also been previously noticed when a broad fraction of oxidizer particles was used.

69. Vilyunov, V. N., and O. B. Sidonskiy. The problem of igniting condensed systems with radiation energy. Fizika gorennya i vzryva, no. 4, 1965, 39-43.

The ignition of a solid propellant induced by light irradiation was analyzed using a simple propellant model. It was assumed that a constant light flux incident on the propellant surface accelerates the chemical reaction which leads to heating of the surface layers; after expiration of a certain period, the light irradiation is stopped and an adiabatic induction period starts; after the induction period, the propellant either ignites or is extinguished depending on the surface temperature. Analysis of the temperature variation under these conditions yielded temperature vs time curves for various propellant parameters. The curves show either extinction or transition to normal combustion. An interesting result of the analysis was that the burning velocity during transition to normal combustion fluctuates with damped oscillations. Two formulas for calculating the induction period were derived.

70. Yevstigneyeva, Ye. V., and G. O. Shmyreva. Heat of combustion of cyclopentadienylmanganese tricarbonyl. Zhurnal fizicheskoy khimii, v. 39, no. 4, 1965, 1000-1002.

The following experimental value of the heat of combustion of pure cyclopentadienylmanganese tricarbonyl was obtained by burning the latter in a calorimetric bomb at an oxygen pressure of 30 atm:
 $\Delta H_{\text{comb}}^{\circ} = -922.1 \pm 1 \text{ kcal/mole}$. This value is an average from 8 tests with 2 specimens of cyclopentadienylmanganese tricarbonyl containing 47.00% C, 2.15% H, 25.55% Mn, and 25.8% O. The calculated value of the heat of formation of $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ was $-125.5 \pm 1 \text{ kcal/mole}$.

71. Zakharov, Yu. A., and G. G. Savel'yev. Changing the physicochemical properties of solids by means of admixtures. Part 6. Role of contact phenomena in the catalysis of thermal decomposition of solids by semiconductor admixtures. *Kinetika i kataliz*, v. 7, no. 1, 1966, 55-61.

The effect of heterophase semiconductor impurities having donor-acceptor properties (NiO , Cu_2O , ZnO , CdO , Bi_2S_3 , Co_2O_3 , Fe_2O_3 , Ag_2S) on the rate of thermal decomposition of ionic salts (PbN_6 , KClO_4 , NH_4ClO_4 , $\text{Ag}_2\text{C}_2\text{O}_4$, and AgN_3) was studied. The heterophase catalysis of solid state reactions is treated in relation to the contact phenomena at the boundary between the catalyst and the reacting solid. The effects are correlated with the reaction mechanism of thermal decomposition. It is shown that if the rate of the process is determined by the electronic step, this rate can be changed by shifting the Fermi level in the crystals of the substance undergoing decomposition. The data indicate that by obtaining information on the rate-determining step of thermal decomposition and by measuring the electronic work function for the substance under consideration, one can alter the rate of decompo-

sition of solid ionic compounds in the desired direction with the aid of mechanical impurities of known work functions.

72. Zel'dovich, Ya. B. The burning velocity of powder under variable pressure. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 3, 1964, 126-138.

The effect of the pressure gradient on the burning velocity of black powder was studied theoretically. Equations are derived for determining the burning velocities of the powder under various conditions. The following cases are considered: a steady combustion regime, combustion under the conditions of a rapid and a slow pressure increase, and the burning and extinguishing of powder at a pressure decrease. The criteria for steady combustion and for combustion under the conditions at a rapid pressure increase are also presented graphically. It is concluded that the higher the initial powder temperature, the lower the final pressure will be prior to extinction.

73. Zenin, A. A. Microthermocouple heat transfer in the combustion of condensed substances. Zhurnal prikladnoy mekhaniki i tekhnicheskoy fiziki, no. 5, 1963, 125-131.

The requirements that must be satisfied by the parameters of a thermocouple (form, thickness, etc.) in order to guarantee a minimum distortion of the temperature profile are studied. Heat transfer between the thermocouple and the condensed and gaseous media was studied and then the errors in the thermocouple measurements were estimated. In particular, it is shown that the sealing of the thermocouple "at an angle" can actually lead to large errors in temperature measurements and serious distortion of the form of the temperature profile.

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