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THERMAL DECOMPOSITION OF LEAD AZIDE  
PREPARED UNDER VARIOUS CONDITIONS

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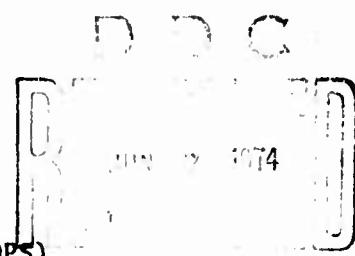
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ABSTRACT:

The effect of various factors on the thermal decomposition rate of lead azide in solid solutions with divalent copper added, was studied under vacuum in a weighing unit and in an automatic differential unit.  $PbN_6$  was prepared by two methods producing small and large azide crystals. The data demonstrate that both production conditions and experimental conditions, associated with the presence or absence of moisture and carbon dioxide in the air and of the copper impurities, have effects ranging from peaceful to explosive on thermal decomposition of lead azide.

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## Experimental Portion

As is well-known, the properties and, especially, the thermal stability of crystalline solids depend to a considerable extent on the conditions of their production: supersaturation, production rate of preparation, media, precipitation temperature, particle size, aging and introduction of impurities into the lattice [1, 2].

We carried out investigations on the effect of some of the conditions enumerated on the rate of thermal decomposition of lead azide, in solid solutions of lead azide, with additions of divalent copper. Thermal decomposition was studied under various experimental conditions:

a) By means of a MacBain balance, in the unit described in [3]; pressure was maintained unchanged in the reaction vessel ( $\sim 2 \cdot 10^{-2}$  mm Hg), as a result of continual removal of gaseous decomposition products in the course of process;

b) In an automatic differential unit; in this case, the preparations were aged, under an initial pressure of  $\sim 10^{-5}$  mm Hg in the system.  $\text{PbN}_6$  decomposition curves obtained in the weighing unit are presented in Fig. 1. As is evident from the curve, change in the method of production appreciably changes the thermal stability of  $\text{PbN}_6$ . In this case, the fine crystal azide, obtained by rapid mixing of 0.2 N solutions of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaN}_3$  (curve 1), is decomposed considerably more slowly than large crystal  $\text{PbN}_6$ , obtained from an ammonium acetate solution by slow precipitation, by the method of Miles [4].

The experiments carried out showed that the nature of the kinetic decomposition curve for pure lead azide (preparation 1) depends on the conditions for conducting the test. By conducting the tests in the weighing unit, the rate of the process proved to be at a maximum in the initial stage of the reaction, and it decreased continually during the process. Observation of decomposition in high vacuum showed, on the other hand, that S-shaped decomposition curves are produced in this case and, besides, the latter method permits the decomposition of the basic lead carbonate to be recorded, giving an initial maximum in the rate-time coordinates of the process. As was

pointed out in work [6], well-aged  $PbN_6$  crystals always have a film of basic lead carbonate on the surface, as a result of which the decomposition process is accelerated in the initial stage.

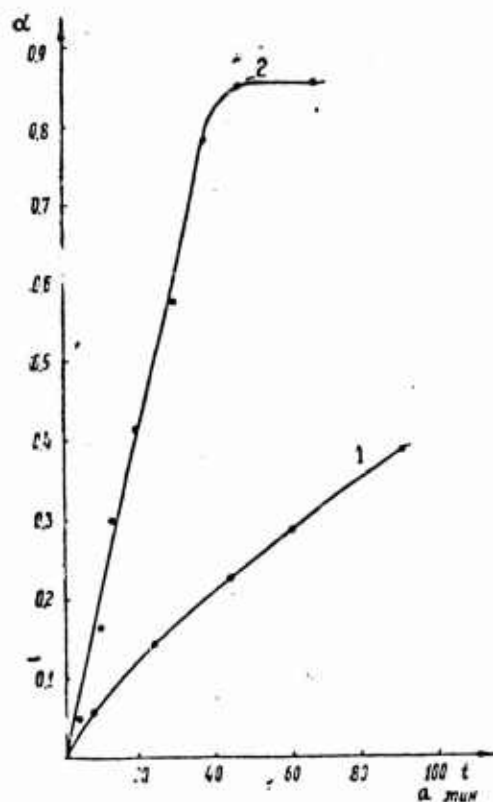


Fig. 1. Effect of method of production on decomposition of lead azide: 1. thermal decomposition, at  $240^{\circ}\text{C}$ , of lead azide produced by rapid mixing of  $0.2\text{ N Pb}(\text{NO}_3)_2$  and  $\text{NaN}_3$  solutions; 2. thermal decomposition, at  $235^{\circ}\text{C}$ , of large-crystal lead azide produced by slow precipitation from ammonium acetate solution.

Key: a. minutes

The pure  $\text{PbN}_6$  synthesis medium also appreciably effects the trend of the kinetic curves in thermal decomposition of  $\text{PbN}_6$  (Fig. 3). As is seen from the figure, in precipitation of  $\text{PbN}_6$  from a medium containing 0.5 g  $\text{CH}_3\text{COOH}$ , the value of the carbonate peak decreases and, with 2 g  $\text{CH}_3\text{COOH}$ , it is not observed at all.

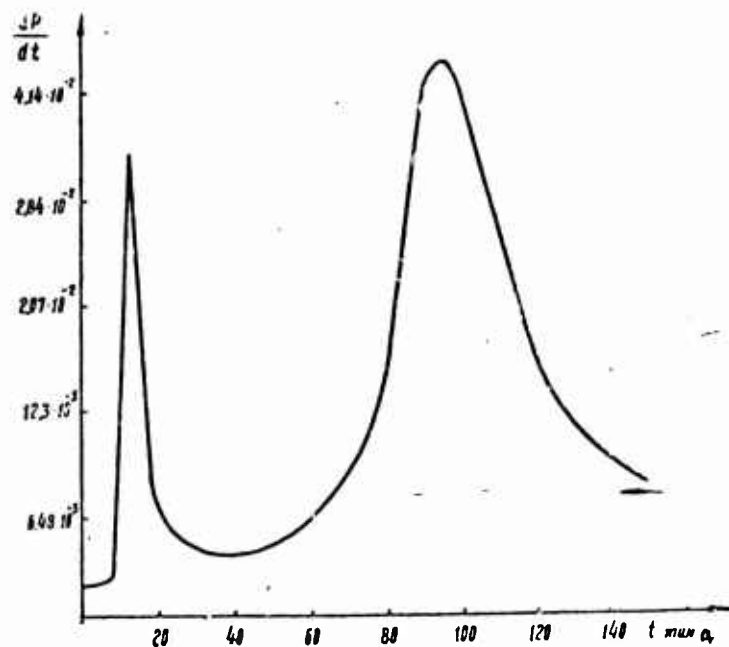


Fig. 2. Effect of test conditions on trend of kinetic curve; thermal decomposition of  $\text{PbN}_6$  in volumetric unit at  $280^\circ\text{C}$ .

Key: a. minutes

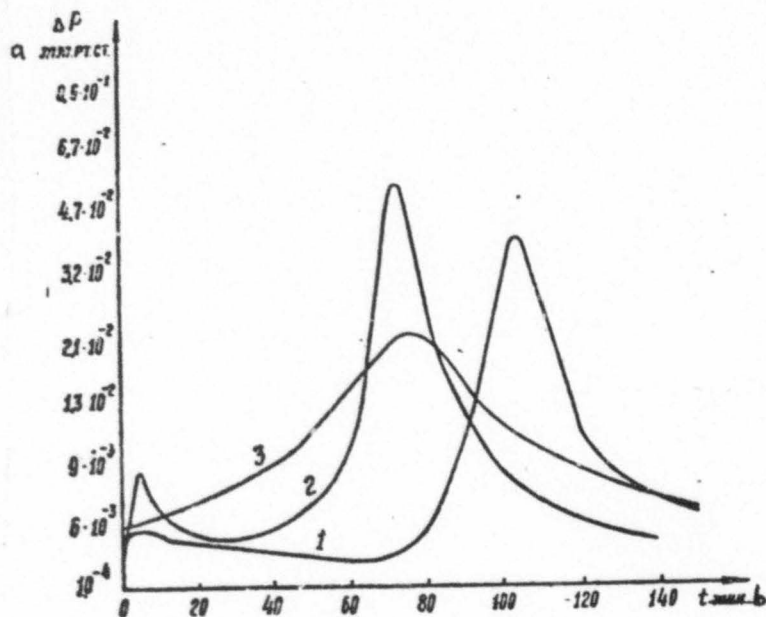


Fig. 3. Thermal decomposition of  $PbN_6$  produced from solutions containing various quantities of  $CH_3COOH$ : 1. 0.5 g  $CH_3COOH$ ,  $t_{dec} = 270^\circ C$ ; 2.  $PbN_6$  without acid,  $t_{dec} = 275^\circ C$ ; 3. 2 g  $CH_3COOH$ ,  $t_{dec} = 270^\circ C$ .

Key: a. mm Hg  
b. minutes

Previous research [7] has shown that divalent copper ions can be fixed in the  $PbN_6$  lattice, forming solid intrusion solutions. We introduced  $Cu^{++}$  ions into the  $PbN_6$  lattice, in the process of lead azide synthesis by two methods:

- 1) By slow mixing (stream into stream) of 0.2 N  $Pb(NO_3)_2$  and  $NaN_3$  solutions, with calculated amounts of 0.2 N  $Cu(NO_3)_2$  solution;
- 2) By rapid mixing of the initial solutions.

Solid  $PbN_6$  solutions, with calculated  $Cu^{++}$  contents of 5, 10 and 15 mole %, were produced by the first method.

They were produced by the second method with  $Cu^{++}$  contents of 2, 4, 6, 8 and 10 mole %.

The effect of the method of precipitation of solid solutions on the effect of impurities can be seen by comparison of Figs. 4 and 5. The change in thermolysis rate of  $PbN_6$  with  $Cu^{++}$  additives in preparations produced by the first method are shown in Fig. 4, and in Fig. 5 by the second method of synthesizing them. In the latter case, in distinction from the first, slowing down of  $PbN_6$  thermolysis by  $Cu^{++}$  additives does not occur in direct relation to the amount of additive introduced, but it has a maximum

value with introduction of 4 - 6 mole %  $\text{Cu}^{++}$ , and with an impurity content of 10 mole %, the preparation explodes (calculated amounts of additive were reduced everywhere and analysis of its content in the crystals was not carried out).

## Discussion of Results

There are three types of decomposition curves for exothermic solid phase reactions, proceeding with formation of a solid reaction product and a gas [8],  
 $A_s + B_s + C_{\text{gas}}$ :

1) Decomposition with the greatest speed observed at the start of decomposition. In this case, the rate of formation of nuclei is high in the initial period, and the surface is almost instantly covered with a film of solid product;

2) The presence of an induction period, when the rate of nucleus formation is low;

3) A rapid, but negligible, emission of gas in the initial heating period and subsequent acceleration of the reaction, as in the second case.

The type a curve is characteristic of lead azide [8], but other types of decomposition curves are possible [6]. We obtained all three types of curves (Figs. 1, 2, 3), in which it turned out that the shape of the kinetic curve for  $\text{PbN}_6$  is determined to a great extent by the experimental conditions. The difference in the curve shapes can be explained by the presence of two lead azide decomposition mechanisms [9]. There is some work confirming this point of view. Thus, it has been shown by X-ray and chemical analysis, as well as on the basis of analysis of the kinetic curve types [10], that thermolysis of lead azide in air, at temperatures of 150, 175 and 200°, takes place through several intermediate phases, probably in the diffusion region. We calculated the apparent activation energies for the data presented in work [10], and we found that it is relatively low ( $\sim 11$  kcal/mole). This value differs from data of other works [6, 11, 12], in which values from 23 to 52 kcal/mole were found. The low activation energy confirms the probable diffusion nature of the process.

In work [9], the authors draw the conclusion of the possibility of two lead azide decomposition mechanisms, either by the normal reaction



at high temperature and in the absence of moisture, or through basic lead azide in the presence of traces of moisture. The latter mechanism is a diffusion one. The thermal decomposition of pure  $\text{PbN}_6$  is represented in curve one, Fig. 1, and the trend of the curve is characteristic of a diffusion decomposition mechanism. The initial acceleration of the kinetic curve can be explained by the presence of basic lead carbonates [6] in the  $\text{PbN}_6$ . The trend of curve two indicates the possibility of  $\text{PbN}_6$  decomposition by another mechanism, with a short induction period and considerable subsequent acceleration. In both cases, the decomposition was carried out in the

weighing unit, at  $P \sim 10^{-2}$  mm Hg. In the first case, the small-crystal  $PbN_6$  preparation, obtained from water solutions, having a larger surface than the large-crystal one, produced from ammonium acetate (as in the latter case), is subject to a great extent to the effect of moisture and  $CO_2$  of the air, with formation of basic carbonates, which give a large number of nuclei. Consequently, the difference in decomposition mechanism can be observed with various methods of production of one and the same preparation.

$PbN_6$  thermal decomposition experiments, carried out in the volumetric unit (Figs. 2, 3), indicate that the conditions under which the experiment is carried out effect the type of the  $PbN_6$  decomposition curve. A type b curve is realized for lead azide only under a higher vacuum: decomposition begins at a pressure of  $\sim 1 \cdot 10^{-5}$  mm Hg, and it proceeds at a pressure of  $10^{-3}$ - $10^{-2}$  mm Hg, in which the decomposition temperature increases considerably. In all probability, not only the effect of water vapors, which, as a number of works has shown [6, 9], can change the trend of the  $PbN_6$  thermolysis curve, but change in heat transfer conditions between the substance and the surrounding medium shows up and, since lead azide decomposition proceeds with evolution of heat, this should affect the reaction rate. In our experiment, the heat transfer conditions change considerably, not only as a consequence of air pressure differences during thermal decomposition, but also owing to the different constructions of the weighing and volumetric units: in the volumetric unit, heat removal is accomplished basically by way of contact with the metallic, heated portion of the unit, and only by means of diffusion of gases and radiation in the weighing unit. As a result of these differences, thermal decomposition in the volumetric unit proceeds peacefully at those temperatures (around  $300^\circ C$ ), at which an explosion takes place in the weighing unit. In this manner, if it is assumed, following the authors of [9], that  $PbN_6$  decomposition proceeds by two mechanisms, it also should be assumed that, at low temperatures, lead azide decomposes by the diffusion mechanism, through the basic carbonates having low activation energy, and, at high temperatures, by the normal reaction with high activation energy. (This holds true under the given experimental conditions.)

In the weight unit, decomposition of small-crystal preparations by the second mechanism could not be observed, since the preparation explodes, as a consequence of evolution of heat, owing to poor heat removal, as soon as the rate of the process



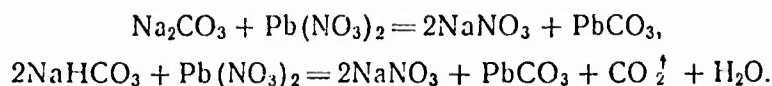
becomes sufficiently high.

The appearance of an initial peak (Fig. 3) in thermal decomposition of  $PbN_6$  in the volume unit can be explained by the presence of impurities having a lower decomposition temperature than  $PbN_6$ .

The following salts may be present as such impurities:

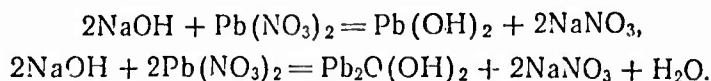
- 1) Lead acetate, forming as a result of the exchange reactions





the salts  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  are present as impurities in sodium azide, which is the initial reagent in  $\text{PbN}_6$  production. It is highly probable that lead acetate is formed in the surface layer of  $\text{PbN}_6$ , as an effect of moisture and carbon dioxide in the air. Addition of acetic acid to the sodium azide solution leads to decomposition of sodium carbonate and bicarbonate and, thereby, reduces the amount of lead acetate in  $\text{PbN}_6$ , which is indicated by a decrease in the initial peak in curve three;

2) The second possible reason for the appearance of an initial peak in thermal decomposition of  $\text{PbN}_6$  is the presence of lead hydroxide impurities  $\text{Pb}(\text{OH})_2$  or  $\text{Pb}_2\text{O}(\text{OH})_2$ , which have a decomposition temperature in air of  $145^\circ\text{C}$  and which are highly soluble in acetic acid. The formation of the hydroxides can proceed according to the reaction



Alkali can be present in the form of an impurity in sodium azide ;

3) It also is possible that basic lead salts, in particular  $\text{PbO}\cdot\text{PbN}_6$ , together with lead carbonate, emerge as the impurities giving the initial peak. These salts have been studied little, and it is only known that their formation in  $\text{PbN}_6$  is connected with the effect of moisture and carbon dioxide in the air [9, 10].

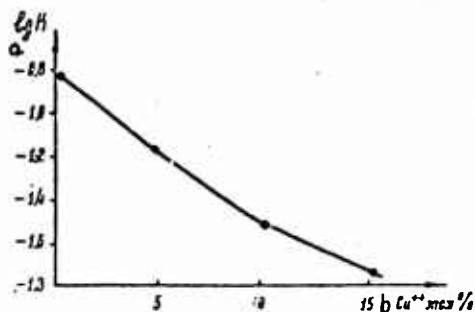


Fig. 4.  $\text{PbN}_6$  thermal decomposition rate constants vs. amount of  $\text{Cu}^{++}$  additive; preparations were produced by slow mixing of initial 0.2 N solutions.

Key: a. log. K  
b. mole %  $\text{Cu}^{++}$

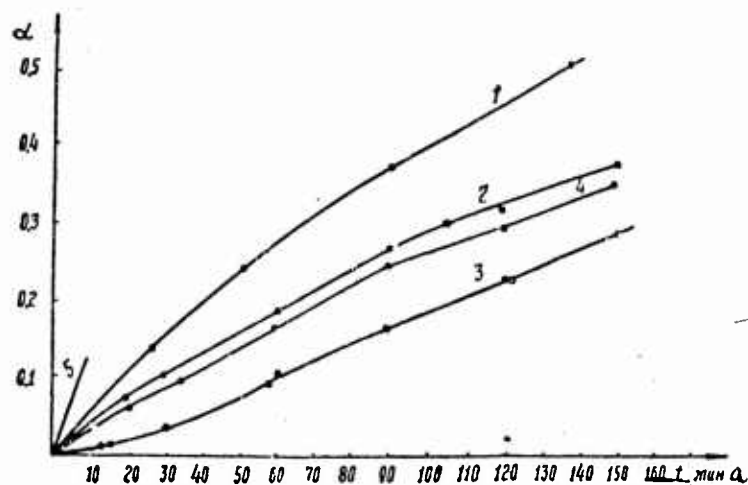


Fig. 5. Thermal decomposition of  $PbN_6$  with  $Cu^{++}$  additives at  $240^\circ C$ : 1. pure  $PbN_6$ ; 2.  $PbN_6$  with 2 mole %  $Cu^{++}$ ; 3.  $PbN_6$  with 4 mole % Cu and  $PbN_6$  with 6 mole % Cu; 4.  $PbN_6$  with 8 mole % Cu; 5.  $PbN_6$  with 10 mole % Cu; preparations were produced by rapid mixing of 0.2 N solutions.

Key: a. minutes

The mechanism of action of homophase  $Cu^{++}$  impurities on thermal decomposition of lead azide have been described in work [13]; therefore, we will not dwell on it. The cause of change in effectiveness of the action of impurities (Figs. 4, 5), depending of method of production of the preparation, may be change in amount of impurity included in the crystal lattice.

Further research is required for conclusive explanation of the cause of this behavior of solid solutions.

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