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EFFECT OF IMPURITIES ON EXCITATION AND
DETONATION PROGRESSION IN SOME INORGANIC
PRIMING AZIDES

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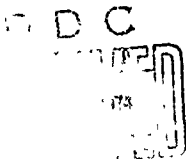
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ABSTRACT: Shock sensitivity and detonation rate were studied in the following systems: lead azide-silver azide, in lead azide-rich corners of the system lead azide-copper azide(II), and in the silver azide-rich corners of the system silver azide-copper azide(II).



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Introducing impurities into inorganic initiating azides is a powerful means of both modifying several of the most important characteristics of slow thermal decomposition, photolysis, and radiolysis [1,2], as well as studying the mechanisms of these processes. In studying the effect of impurities on radiolysis, photolysis, and thermal decomposition, the role of electronic factors in the buildup of slow decomposition was clarified and several methods of directed modification of several properties of initiating explosives were developed. Therefore it was of interest to find the effect of impurities on processes of the initiation and progression of detonation in order to clarify the mechanism of fast-action decomposition and to determine the explosive properties of substances modified with additives.

We determined the shock sensitivity and detonation rate for initiating compositions in the following systems: lead azide-silver azide ($\text{Pb(N}_3)_2$ -- AgN_3), in the lead azide-rich corners in the system of lead azide with copper azide(II) ($\text{Pb(N}_3)_2$ -- $\text{Cu(N}_3)_2$), and in the silver azide-rich corners in the system of silver azide with copper azide(II) (AgN_3 -- $\text{Cu(N}_3)_2$), as well. The compositions were synthesized by combining 0.2 N solutions of the corresponding salts: NaN_3 , $\text{Pb(NO}_3)_2$, $\text{Cu(NO}_3)_2$, and chemically pure AgNO_3 . The compositions were dried in vacuum and stored over P_2O_5 . Measurements were taken for the compositions after they had been pressed to a density of 1.8 g/cm^3 , identical in all experiments.

Shock sensitivity was determined with a K-4-44-1 piledriver with the needle geometry opposite the "Russian breakthrough" plane, that is, for ten samples at each point. The detonation rate was determined by photographic recording on a SPR-L high-speed photo-register at a scanning speed of 45,000 frames per minute. Samples used in measuring the detonation rate were prepared by pressing the initiating composition into a cellophane capsule 0.1 mm thick, 5 mm in diameter to a base of 2 cm with a constant weighed sample. The recorded frames bore the appearance of straight sharp lines without a noticeable region of detonation acceleration.

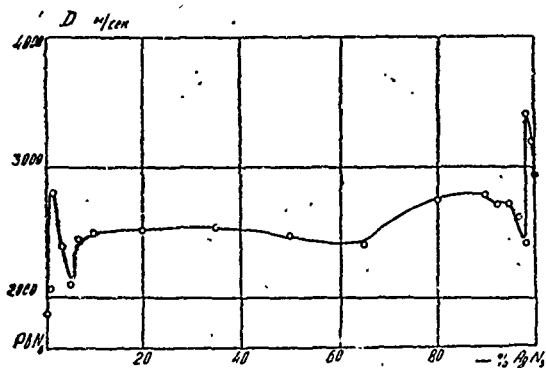


Fig. 1. Dependence of detonation rate on composition in the system $Pb(N_3)_2-AgN_3$
KEY: A -- m/sec

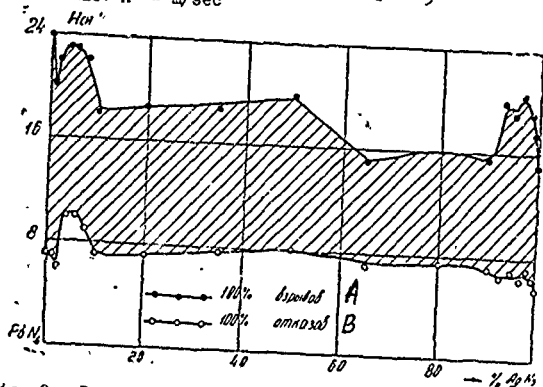


Fig. 2. Dependence of shock sensitivity on composition in the system $Pb(N_3)_2-AgN_3$
KEY: A -- 100% explosions B -- 100% failures

The precision of detonation rate determination was 50 m/sec, and five determinations were made for each composition.

Fig. 1 presents the function of the detonation rate in the system $\text{Pb}(\text{N}_3)_2\text{--AgN}_3$. The composition was specified based on the composition of nitrate solutions prior to coprecipitation. The significant rise in the detonation rate in the initial sections of the plot must be noted, that is, in the area of solid solution formation. With the breakdown of the solid solution, a decrease in the detonation rate is observed. In the region in which the mechanical mixture $\text{Pb}(\text{N}_3)_2(\text{Ag}^+)$ and $\text{AgN}_3(\text{Pb}^{2+})$ exists, there is a monotone rise in the detonation rate in the middle of the diagram.

The dependence of shock sensitivity in this same system is shown in Fig. 2. The corridor of incomplete action of the compositions is hachured. Here a descent in the curve is observed in the region of solid solution formation, that is, a rise in sensitivity and then, with increasing breakdown of the solid solutions, a drop in sensitivity; the course of the shock sensitivity curve as well as the course of the detonation rate curve is monotone in the region of mechanical mixtures. Noteworthy is the fact that the climb in the detonation rate corresponds to the rise in shock sensitivity. A comparison of shock sensitivity in the corner of the diagram rich in $\text{Pb}(\text{N}_3)_2$ of the system $\text{Pb}(\text{N}_3)_2\text{--Cu}(\text{N}_3)_2$ with the detonation rate in this system is shown in Fig. 3.

The rise in the detonation rate with increase in the impurity content occurs more smoothly than in the corners of the system $\text{Pb}(\text{N}_3)_2\text{--AgN}_3$. The increase in the detonation rate also corresponds to a rise in the shock sensitivity of the compositions. The character of the functions of the detonation rate and the shock sensitivity of the corner rich in AgN_3 in the system $\text{AgN}_3\text{--Cu}(\text{N}_3)_2$ (Fig. 4) differs from that in the above-described systems: a sharp drop in the detonation rate is observed in the region of low impurity content. The increase in shock sensitivity corresponds to the increase in detonation rate, while the decrease in the detonation rate corresponds to the decrease in shock sensitivity, as in the systems $\text{AgN}_3, \text{Pb}(\text{N}_3)_2\text{--Cu}(\text{N}_3)_2$.

Compositions rich in copper azide(II) were not studied owing to the extreme danger of handling them: arbitrary explosions occurred at all stages of the processing of compositions and samples.

We had already met these patterns of variation in detonation rate; the compositions were prepared by different methods and from different starting preparations.

In discussing these results, it must be noted that owing to our efforts to keep the macroscopic density of the samples constant, it can be assumed

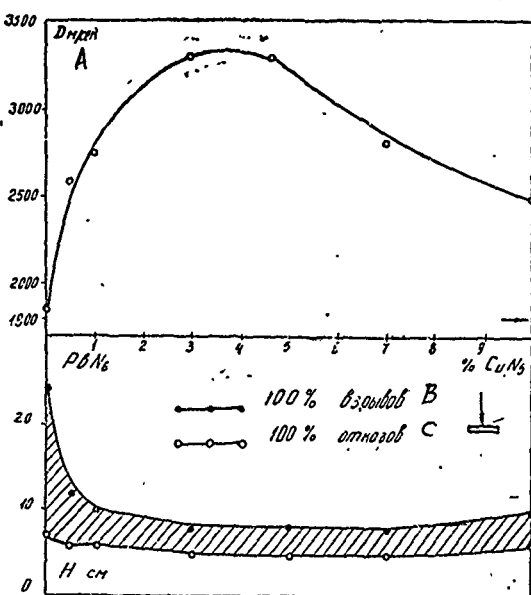


Fig. 3. Comparison of the dependence of detonation rate and shock sensitivity on composition in the system $Pb(N_3)_2-Cu(N_3)_2$
 KEY: A -- m/sec B -- 100% explosions
 C -- 100% failures

that the resulting changes in detonation when microimpurities were introduced are not determined by the factor of macroscopic density. The following can include some of the other causes:

- 1) microscopic or roentgenographic density of individual microcrystals can have a strong effect if the detonation buildup occurs without the participation of air gaps [5];
- 2) introducing impurities can modify the dimensions of individual microcrystals, however direct observation showed that marked change in the crystal habit occurs only in the system $Pb(N_3)_2-Cu(N_3)_2$, where for small amounts of impurity the alpha-form of $Pb(N_3)_2$ converts into the beta-form of $Pb(N_3)_2$;

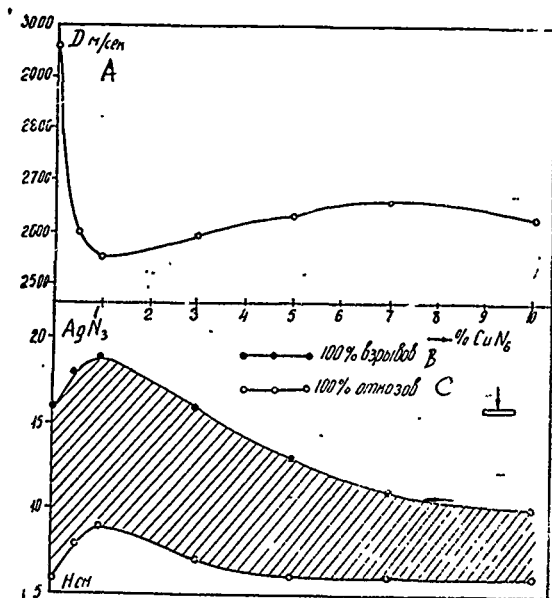


Fig. 4. Comparison of the dependence of detonation rate and shock sensitivity on composition in the system $\text{AgN}_3\text{-Cu(N}_3)_2$
 KEY: A -- m/sec B -- 100% explosions
 C -- 100% failures

3) the effect of impurities (especially in small amounts) cannot markedly modify the energetics of process buildup, therefore one of the possible causes of this effect can be the degree of caution in labelling the effect of variable thermal stability of compositions and, therefore since change in thermal stability was explained by us from the standpoint of electronic excitation processes [2], citing the effect of impurities on the electronic structure of a substance.

However, modifying the electronic structure of an explosive can -- according to the viewpoint in [3] -- directly affect the conditions of excitation and detonation buildup. For example, in the case of initiating inorganic azides, the effect of electron donors and acceptors on the electronic

excitation of the azide radical N_3^0



can markedly affect the kinetics of decomposition occurring via the equation



However, the current unavailability of data on the zone structure of the systems described above prevents us from discussing this problem in detail. We must once again stress the fact that there is a parallel between the detonation rate and shock sensitivity, which evidently confirms the viewpoint prevailing in explosion physics that both these processes are essentially thermal in character [5].

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