

Initiation of explosive reactions in high energy materials with nanosize additives by a high-voltage discharge

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Abstract

The results of experimental and theoretical studies of the effect of nanosize inert additives on the threshold voltage of initiation of explosive reactions in high energy materials (HEM) are presented. Two HEMs were studied: (i) based on potassium picrate and (ii) based on the red lead. The particle size for both HEMs was $\sim 100 \mu\text{m}$. As nanosize additives, we used: (i) copper nanopowder with particle sizes of 100-130 nm; (ii) detonation nanodiamonds with particle sizes of less than 100 nm and (iii) KDB silicon nanopowder with a particle size of about 100 nm. It was found that (i) the electrical breakdown of the powder composition is the primary phenomenon, while the initiation of HEM is a consequence of this breakdown; (ii) when adding the nanosize additives to the HEMs, a significant decrease in the initiation voltage is observed; herewith the larger the content of the nanosize additive the more decrease in the initiation voltage; (iii) the higher the rate of voltage rise in the experiment, the greater the breakdown voltage of HEM with nanosize additives. A model of electrical breakdown of HEM with nanosize additives is considered. It is shown that the dependence of the breakdown voltage on the content of nanoadditive is connected with the inertness of formation of percolation clusters of nanoparticles in the electrostatic field and with a finite rate of voltage rise. The theoretical dependence is in agreement with the available experimental data.

Keywords: high energy materials, nanosize additives, electrical breakdown, breakdown voltage

1. Introduction

The initiation of high energy materials (HEMs) (in particular explosives) by a high-voltage electrical discharge is of interest, both from the point of view of developing new initiating devices, and from the point of view of the explosion safety.

The advantage of this method of initiating an explosive is its fast performance (a few microseconds), while its disadvantage (at present) is high values of the voltage required for initiation. Experimental investigations¹⁾ were aimed at estimating the effect of the conducting copper nanopowder on the sensitivity to a high-voltage electrical discharge in a high energy composition of a low-sensitivity

fine-grained (mean size of particles is about $5 \mu\text{m}$) FOX-7 explosive. It was found that addition of 15% by mass of the copper nanopowder reduces the initiation threshold of FOX-7 explosive from 15 kV to 7.5–9.0 kV. Based on the experimental data¹⁾, a model of surface percolation as a reason of the electrical breakdown in low-sensitive fine-grained powder explosives with nanosize additives was developed²⁾.

The experiments^{1), 2)} were performed with metal (copper) nanopowders, which exhibit a high capacity for agglomeration and, similar to all nanopowders, over time they are coated with an oxide film, as a result of which they lose their conductive properties. Moreover, the

experiments^{1),2)} were conducted with a parallel arrangement of electrodes although in actual initiating devices, the pointed electrodes are usually used.

The goal of this study is to investigate the effect of various nanosize additives on the breakdown voltage for two coarse-grained powder HEMs in a device with pointed electrodes.

2. Experimental

In this study, we examined two HEMs which were manufactured in the St. Petersburg State Technological Institute (Russia): the first based on potassium picrate (hereinafter referred to as HEM-1) and the second on the basis of red lead (HEM-2). Both HEMs are powders with a particle size of the order of 100 μm .

The experiments were carried out both for pure powdered HEMs and for powdered HEMs with nanosize additives.

As nanosize additives, we used the following powders: (i) copper nanopowder with an initial particle size of 50–70 nm, but coated with an oxide film 50–60 nm thick, so that the powder was absolutely black and had a grain size of 100–130 nm (hereinafter, this powder will be referred to as CuO); (ii) detonation nanodiamonds (DNDs) with a particle size smaller than 100 nm; and (iii) KDB silicon nanopowder with a particle size of about 100 nm.

The mixtures of HEM-1 with CuO, DND or KDB silicon nanopowder and HEM-2 with CuO were stirred in a liquid non-polar solvent (toluene) using an ultrasonic Sonicator processor until they were evenly colored, then placed into an organic glass (insulator) container (Figure 1).

The charges obtained in this way were of almost bulk density and had a mass in the range 0.7–1.0 g.

In order to answer the question of what is primary: an electrical breakdown of the mixture, which entails the initiation of explosive conversions in a high energy material, or the initiation of an explosive conversions in a high energy material that entails an electrical breakdown, the experiments were also performed with an inert powder, quartz sand, with a mean particle size of about 100 μm . The quartz sand had a polydisperse composition. Similar to HEM-2 compound, the experiments were carried out both for pure quartz sand and for mixture of quartz sand with CuO nanopowder.

The electric circuit diagram of the experiment is shown in Figure 2.

The experiments were conducted in a room under constant temperature, humidity and pressure. A static voltage was smoothly increased in the range 0–10 $\text{kV}\cdot\text{s}^{-1}$ at a rate $\dot{U} = 1 \text{ kV}\cdot\text{s}^{-1}$. At some voltage, a spark breakdown initiated between the electrodes caused excitation of the explosion in the high energy mixture. The breakdown voltage was determined with the help of a kilovoltmeter. Apart from the above rate of voltage elevation, experiments on determining the breakdown voltage were carried out in three cases with a rate $\dot{U} = 2 \text{ kV}\cdot\text{s}^{-1}$.

In order to determine the characteristics of our experimental setup, we initially measured the electrical breakdown in pure air for the electrodes used.

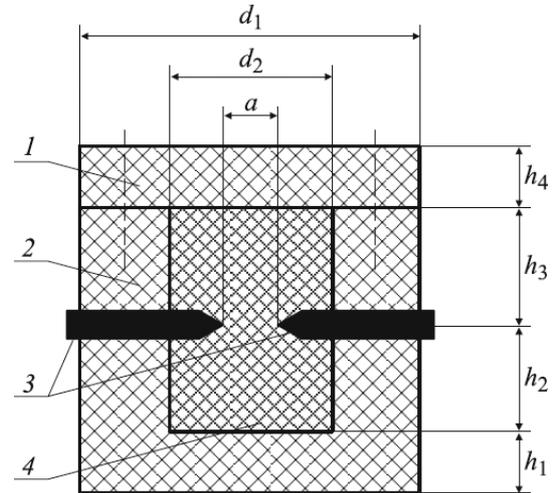


Figure 1 Cylindrical container with a high energy mixture: (1) lid; (2) casing; (3) electrodes; (4) high energy mixture (dashed lines show the regions of fixation of the lid). $d_1 = 20 \text{ mm}$, $d_2 = 10 \text{ mm}$, $h_1 = 5 \text{ mm}$. ($h_2 + h_3$) = 10 mm; two steel point electrodes of diameter 3 mm were used; $h_2 = 5 \text{ mm}$. The container casing was closed with an organic glass lid of thickness $h_4 = 5 \text{ mm}$, which was fixed to the casing with two bolts. The separation between the electrodes was $a = 3 \text{ mm}$.

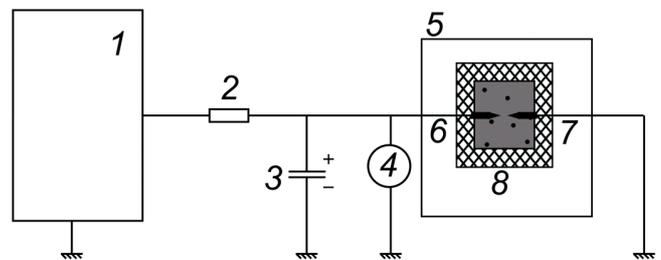


Figure 2 Electric circuit diagram of the experiment: (1) high-voltage power supply; (2) charging resistance; (3) charging capacitance (0.5 μF); (4) kilovoltmeter; (5) chamber; (6) high-voltage electrode; (7) earthed electrode; (2) container with a high energy mixture.

It was found that the breakdown voltage in the air gap of width 3 mm between pointed electrodes was $U_a = 8.0\text{--}8.4 \text{ kV}$. This value is slightly lower than follows from the rated experimental electric strengths of air³⁾ ($\sim 10 \text{ kV}$) for the same air gap between the electrodes (3 mm). The difference is explained by the fact that the electric strength of air was determined with planar electrodes³⁾, while our experiments were performed with pointed electrodes, which led to the local elevation of the electric field strength in the gap and, as a consequence, a lower value of the breakdown voltage.

To verify this conclusion, experiments were carried out with cut electrodes at a fixed distance between them of 3 mm. For this purpose, the tip of the electrodes was cutted to a certain diameter, which varied from 0 to 1.64 mm (both electrodes in the same experiment had the same shape and sizes). This resulted in a monotonous increase in the breakdown voltage of air in our experimental setup from 8 kV to 9.5 kV. Subsequently, all experiments were carried out with pointed electrodes.

After this, experiments were carried out with various powders without nanosize additives. In all these experiments, the rate of voltage rise was $1 \text{ kV}\cdot\text{s}^{-1}$. It was

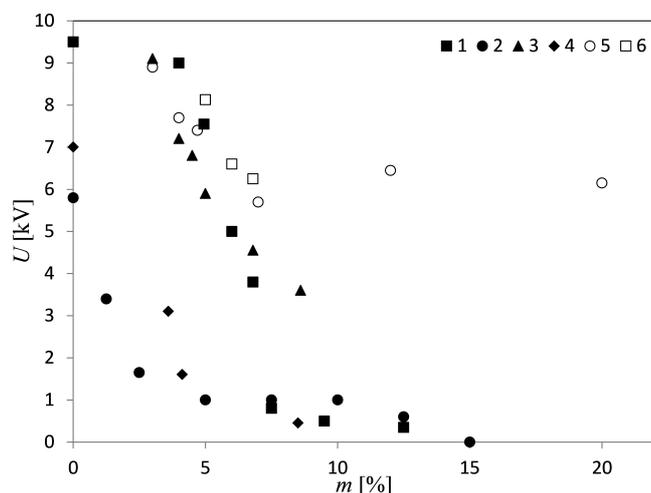


Figure 3 Dependences of the breakdown voltage on the mass fraction of the nanoadditive in the sample for different powders and nanoadditives: 1 and 6 – HEM-1 compound+CuO nanopowder; 2 – HEM-2 compound+CuO nanopowder; 3 – HEM-1 compound +KDB silicon nanopowder; 4 – quartz sand+CuO nanopowder; 5 – HEM-1+DND; data 1-5 correspond to the rate of voltage rise in the experiments $\dot{U} = 1 \text{ kV}\cdot\text{s}^{-1}$; data 6 corresponds to a rate of voltage rise $\dot{U} = 2 \text{ kV}\cdot\text{s}^{-1}$; for composition 5 there is one more point: $m = 36\%$, $U_b = 5.4 \text{ kV}$, which is not shown in the graph for reasons of clarity.

found that the electrical breakdown (initiation) of pure HEM-1 compound occurs at a voltage of $U_0 = 9.5 \text{ kV}$, pure HEM-2 compound occurs at $U_0 = 5.8 \text{ kV}$, and pure quartz sand occurs at $U_0 = 7.0 \text{ kV}$. It is interesting to note that the electrical breakdown of pure HEM-1 compound occurred at voltages greater than the breakdown voltage of pure air, while the electrical breakdown of pure HEM-2 compound and pure quartz sand occurs at voltages much lower than the breakdown voltage of pure air.

We also carried out experiments on the electrical breakdown of pure CuO nanopowder, pure DND and pure KDB silicon nanopowder under the same conditions. The breakdown voltage of pure CuO nanopowder was $U_n = 0.22 \text{ kV}$; for the pure KDB silicon nanopowder, $U_n = 3.5 \text{ kV}$ was obtained; for pure DND, $U_n = 4.25 \text{ kV}$.

Then, experiments were carried out with quartz sand+CuO, HEM-1+CuO, HEM-1+DND, HEM-1+KDB, and HEM-2 + CuO compositions.

Figure 3 shows the values of the breakdown voltages obtained in experiments for various powders with different additives. The data are presented in the form of the breakdown voltage versus the mass fraction of the additive in the powder mixture.

The experimental data (Figure 3) show that the addition of any nanopowder from those considered above reduces the breakdown voltage the more strongly the higher the concentration of the nanopowder in the mixture. The results given in Figure 3 show that various nanopowders reduce the electrical breakdown (initiation) voltage to different levels even for the same baseline powder (HEM-1). With increasing concentration of a nanopowder in the mixture (both for high energy composition and for inert quartz sand), the breakdown

(initiation) voltage tends asymptotically to a certain (generally nonzero) limit that mainly depends on the properties of the nanopowder.

Thus, the breakdown voltages of such different materials as HEM-1, HEM-2 and quartz sand (data 1, 2 and 4, Figure 3) with CuO nanopowder additive tends to close values corresponding to the breakdown voltage of pure CuO nanopowder ($\sim 0.22 \text{ kV}$). At the same time, the breakdown voltage of HEM-1 with the addition of DND asymptotically tends to a level of $\sim 5.4 \text{ kV}$, which is close to breakdown voltage of pure DND.

3. Theoretical

The decrease in the electric strength of a sample when a nanosize powder is added to it is associated with the forced percolation of nanoparticles in a strong electric field, as a result of which a percolate chains are formed in the pores of a coarse-grained powder, having less electric strength than air (see Section 2), over which an electrical breakdown occurs^{2),4)}.

A forced percolation of nanoparticles occurs due to polarization of nanoparticles in electric field. As a result, under the action of dipole attraction and dipole interaction with an external electric field, nanoparticles assemble into clusters extended along the lines of force of the electric field. Over time, the size of these clusters grows and, under certain conditions, a percolate clusters form in the pores of the sample, closing the electrodes, which leads to electrical breakdown.

In this series of experiments, the voltage increases monotonically with time. Taking into account that the process of formation of the percolate clusters occurs in time, the conditions of the electrical breakdown of the sample will depend on the rate of voltage rise. So, if at the moment of formation of the percolation cluster the voltage exceeds the value U_n corresponding to the electric strength of the cluster, then a breakdown of the cluster occurs, which will entail the breakdown of the entire sample. In this case, the breakdown voltage of the sample is equal to the voltage reached at the moment of appearance of the percolation cluster in the system. If at the moment of appearance of the percolation cluster the voltage achieved at the electrodes is less than U_n , then the cluster is an insulator and the breakdown of the sample does not occur at this moment; it will occur with a further increase in voltage, when the voltage U_n will be reached. In this case, the breakdown voltage of the sample will be equal to U_n . If, however, the breakdown voltage of air in the pores of the sample U_0 was reached between the electrodes while the percolation cluster in the system did not have time to form then the sample breakdown will occur at a voltage U_0 , equal to the breakdown voltage of a pure sample without nanosize additives.

Thus, the breakdown voltage of the sample with nanosize additives is determined by the expression

$$U_b = \begin{cases} U_n, U_p < U_n \\ U_p, U_n < U_p < U_0 \\ U_0, U_p = U_0 \end{cases} \quad (1)$$

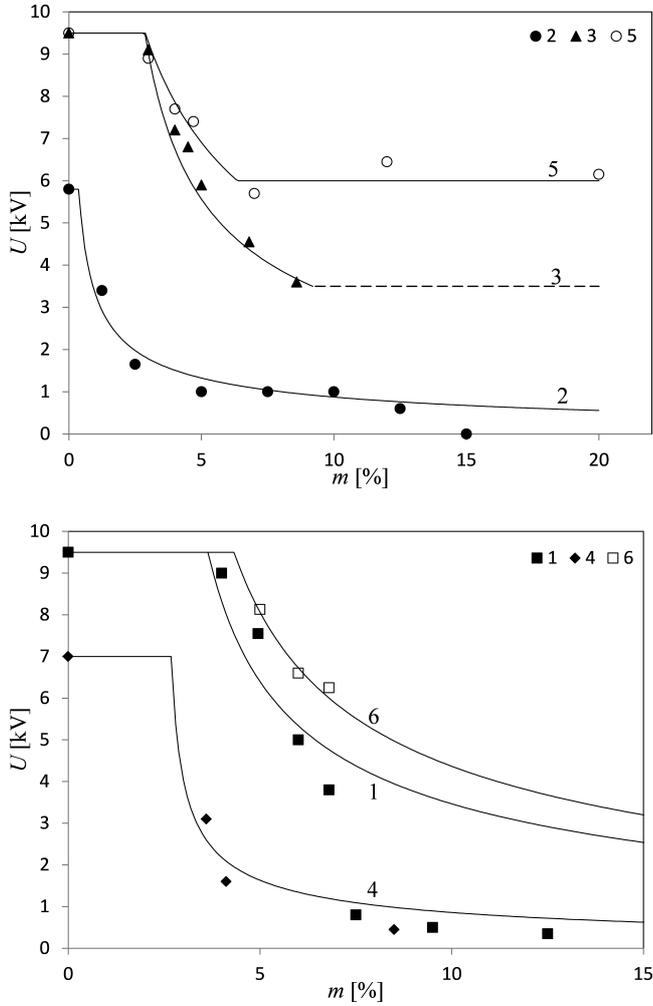


Figure 4 Comparison of experimental data and theoretical dependence Equations (1), (3), and (4). The notations are the same as in Figure 3. Lines 1 and 6: $A = 0.2$; $m_0 = 2.3\%$; line 2: $A = 0.08$; $m_0 = 0$; line 3: $A = 0.2$; $m_0 = 1.5\%$; line 4: $A = 0.06$; $m_0 = 2.5\%$; line 5: $A = 0.3$; $m_0 = 0$. Theoretical predictions, for which there are no experimental data, are shown in dashed line.

where U_p is the voltage achieved at the moment of appearance of percolate cluster in the sample.

Thus, the breakdown voltage of the sample with nanosize additives is in the range $U_n \leq U \leq U_0$ and depends on the rate of voltage rise and on the rate of formation of percolate cluster in the sample.

The breakdown voltage of a coarse powder without nanosize additives is determined by the relation⁴⁾

$$U_0 = \frac{1}{\alpha} \left[1 - \frac{1}{3} (1 - 1/\varepsilon_p) \right] U_a \quad (2)$$

where ε_p is the permittivity of the grain material of the coarse powder; $\alpha \sim 1$ is a coefficient that takes into account the mutual influence of pores in a sample. The voltage between the electrodes at the moment of appearance of the percolate cluster is determined by the relation⁴⁾

$$U_p = AU_0^{2/3} \dot{U}^{1/3} \left(\frac{1-m'}{m'} \right)^{5/9} \quad (3)$$

where A is a constant parameter of the system; m' is the mass fraction of the free nanoparticles in the mixture

which is determined by the expression

$$m' = \begin{cases} 0, & m \leq m_0 \\ m - m_0, & m > m_0 \end{cases} \quad (4)$$

m_0 is the mass fraction of the bound nanoparticles (adhering to the surface of coarse particles and not participating in the formation of a percolate cluster), which is considered to be a constant characteristic of the mixture.

Figure 4 shows a comparison of the theoretical dependences Equations (1), (3), and (4) for the tested powder mixtures with the experimental data shown in Figure 3. Note, that for the content of the additive in mixture 3 of more than 10% for which there are no experimental data, the dependence (1), (3) and (4) is shown by dashed line.

We see that the theoretical dependence Equations (1), (3), and (4) adequately describes the available experimental data for mixtures 2, 3, 4 and 5 in the entire range of the change in the content of the nanosize additive.

At the same time, for the data 1 (HEM-1+CuO) the theoretical Equations (1), (3), and (4) adequately describes the available data only for a relatively small nanopowder content in the mixture ($m < 6.5\%$), but at the same time it correctly predicts an effect of the rate of voltage rise \dot{U} on the the breakdown voltage. Analysis of data 1 shows that when the content of CuO nanopowder in a mixture with HEM-1 exceeds 6.5%, the percolate cluster for some reason is formed very rapidly already at low voltages $U \leq U_p$.

In conclusion, we note that if the percolate cluster has an initial conductivity (i.e., it is a conductor) and appears in the system at voltages less than U_n , then breakdown does not occur; in this case, there will be a smooth discharge of the capacitor. This was observed in experiments with the composition HEM-2+CuO at a CuO nanopowder content of 15% (see Figures 3 and 4). It can be assumed that in this case, for some reason, the contacts between the nanoparticles passed through the metal (Cu) which is the part of CuO nanoparticles.

4. Conclusion

The main results of this study are as follows.

1. The electrical breakdown of a powder composition is a primary effect, while the initiation of the high energy mixture is a consequence of this breakdown.
2. Addition of nanosize additives to the powder HEMs decreases considerably the breakdown (initiation) voltage; the higher the concentration of nanosize additive, the stronger the decrease.
3. The higher the rate of the voltage rise in the experiment, the higher the breakdown voltages for HEM charges with nanosize additives.
4. The model⁴⁾ of electrical breakdown of powder mixtures (both high energy and inert) with nanosize additives, according to which an induced percolation of nanoparticles in strong electric field results in formation of percolate cluster with less electric strength than air filling the pores

between the HEM particles, allows explaining all regularities observed in experiments.

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