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Evolution of Electrical Conductivity of Emulsion Explosives During Their Detonation Conversion

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Abstract: Electrical conductivity of explosion products behind the detonation front of emulsion explosives is measured. The composition of the emulsion matrix and the amount of the additive consisting of sensitizing glass microspheres are varied. The peak value of electrical conductivity for the examined compositions is 0.5–0.05 $\Omega^{-1} \cdot \text{cm}^{-1}$.

Keywords: detonation, emulsion explosive, chemical reaction time, chemical reaction zone, electrical conductivity of explosion products.

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INTRODUCTION

Emulsion explosives (EMXs) are prepared on the basis of a reactive matrix (emulsion), which is not capable of detonation by itself. The ability of the emulsion to detonate is provided by addition of special sensitizers, e.g., thin-walled hollow microspheres made of glass. Being compressed in the wave front, these microspheres collapse, and high local pressures and temperatures of 2500–3000 K are reached [1, 2]. Thus, microspheres serve as nuclei of "hot spots" where the reaction starts [3]. EMXs are widely used in mining [4] and exhibit certain specific features, such as a nonmonotonic dependence of the detonation velocity on density, and an increase in the critical diameter and chemical reaction time with increasing density of compositions [5, 6]. The chemical reaction time estimated on the basis of mass velocity profiles by the electromagnetic method [7, 8], laser interferometry [9], pressure profiles [10], and density profiles behind the wave front [11] lies in the interval 0.5–2.0 μs.

The goal of this study was to measure the electrical conductivity $\sigma(t)$ of explosion products (EPs) behind the detonation front in EMXs and to seek for a correlation between the parameters of the reaction zone and the electrical conductivity profile. To solve this problem, we used a previously developed method of measuring $\sigma(t)$ with a submicrosecond time resolution [12, 13]. Electrical conductivity profiles as functions of time in a wide range of initial EMX densities were obtained and analyzed.

EXPERIMENT

We used emulsion matrices on the basis of an aqueous solution of either a mixture of ammonium and sodium nitrates (AN/SN emulsion) or ammonium nitrate only (AN emulsion); the compositions of these emulsions are listed in the table. For EMX preparation, MS-V hollow glass microspheres produced in Russia were added to the emulsion. The microsphere mass μ was 3–50% above the emulsion mass, e.g., $\mu = 20\%$ means that 0.2 g of microspheres were added to 1 g of the emulsion. The mean microsphere size was 58 μm, the density of loose packed spheres was 0.14–0.15 g/cm^3, and the wall thickness was 0.5–1.0 μm. Using x-ray

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Matrix	Composition, wt.%					Oxygen balance, %	Density, g/cm^3
	ammonium nitrate	sodium nitrate	water	oil emulsifier	paraffin		
AN/SN emulsion	68.25	10.55	15.2	4	2	−2	1.4
AN emulsion	76.9	—	15.2	4	3.9	−12	1.5

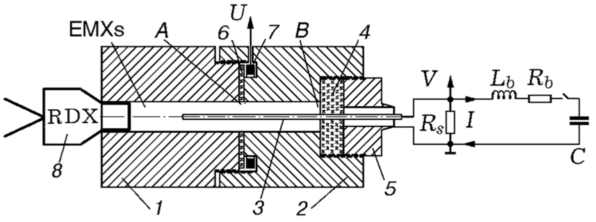

Fig. 1. Electric circuit and experimental cell.

tomography [14], we studied an EMX sample approximately ≈1 mm in size with $\mu = 3\%$ and found that microspheres are uniformly distributed over the volume.

The technique of electrical conductivity measurement and data processing was discussed in detail in [12, 13]; therefore, we give only a brief description here.

The EMX was placed into a coaxial copper cell (Fig. 1). The charge diameter was $b = 8$ mm. The external electrode was composite; its parts *1* and *2* were tightly connected by threading. The internal copper electrode *3* with a diameter $c = 2$ mm was placed into the EMX and was fixed in a PMMA plug *4*, which, in turn, was fixed by a copper bolt *5*. The cavity of the external electrode contained a toroidal coil *7*, which served as a sensor for electrical conductivity measurements. A narrow slit connecting the cavity with the measurement volume of the cell was filled by a dielectric *6*, which was PMMA 0.4–0.7 mm thick. The examined EMX was initiated by RDX with a density $\rho = 1.1$ g/cm^3 through an axial channel 4 mm in diameter in the PMMA plug *8*. The initiator power was varied by changing the RDX charge length from 5 to 25 mm. As a result, the regimes of shock loading of the EMX without detonation development, normal detonation, and overdriven detonation were obtained. The total EMX charge length was 50 mm.

The cell was fed by the current I from a capacitor through a ballast resistance R_b; a shunt R_s was connected parallel to the cell. The feeding voltage $V(t)$ and the coil gauge signal $U(t)$ were measured. The electrical conductivity in the plane of the slit is proportional to the signal from the coil:

$$\sigma(t) = \frac{\ln(b/c)}{2\pi DM}\frac{U(t)}{V(t)}. \qquad (1)$$

Here t is the time that passed after the detonation front bypassed the slit, D is the detonation velocity, and M is the mutual inductance between the coil and the cavity circuit. The signal was corrected to eliminate distortions of $U(t)$ due to coil inductance [13].

The spatial resolution of the system is estimated as one quarter of the thickness of the insulator *6* [13]. The electrical conductivity measurement error was within 20%. By the time when the detonation wave reached the insulator, the detonation front covered a distance of more than four calibers from the initiation point. The detonation velocity D was measured on the base AB approximately equal to 15 mm. The position A corresponds to the instant when the detonation front passes by the slit. The position B corresponds to the instant when the detonation wave reaches the end face of the charge. Given sufficient initiation intensity, all compositions under consideration detonate inside the experimental cell, because the critical diameter of EMX in a strong metal shell (steel) is smaller than 8 mm [15].

Two or three tests were performed for each EMX with fairly reasonable repeatability. The random oscillations on the background of the main signal (see Fig. 6b below) was mainly caused by charge inhomogeneity, which was difficult to avoid for our small charges.

Preliminary Estimates

Under standard condition, the electrical conductivity of a pure emulsion with no sensitizer was approximately $4 \cdot 10^{-8}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ for the AN/SN emulsion and approximately $8.4 \cdot 10^{-8}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ for the AN emulsion. In the case of shock loading of the pure AN/SN emulsion (the mean velocity of the compression wave was 1800 m/s on the base $AB = 30$ mm), the electrical conductivity increased up to $\sigma = 6.6 \cdot 10^{-3}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$, smaller than the values recorded in the detonation wave approximately by two orders of magnitude. After a decrease in pressure, the initial resistance was recovered in ≈40 μs, which indicates that there were no noticeable physicochemical transformations in the pure emulsion under dynamic loading sufficient for initiation of an EMX including a sensitizer additive.

The initial emulsion contains approximately 15% of water whose dissociation could contribute to the electrical conductivity behind the shock wave front. However, even for the pressure of 5–8 GPa behind the shock wave, which is typical for EMX detonation, the electrical conductivity of water is $\sigma < 10^{-3}\ \Omega^{-1}\cdot\text{cm}^{-1}$ [16], which is appreciably lower than the shock conductivity of the emulsion. For this reason, the observed values of the conductivity of EMX explosion products cannot be explained by the contribution of the shock conductivity.

During EMX detonation, hollow glass microspheres disintegrate into submicron fragments. As was shown in [17], the electrical conductivity of glass drastically increases in shock waves; however, in our range of pressures, it does not exceed $10^{-4}\ \Omega^{-1}\cdot\text{cm}^{-1}$, so it can be neglected. As a result, detonation products contain the dielectric, which is almost not involved into chemical reactions and occupies some part of the medium volume. The volume fraction of glass α after microsphere destruction can be estimated as

$$\alpha = \frac{\mu}{\mu + \rho_g/\rho_m},$$

where ρ_g and ρ_m are the glass and matrix densities, respectively. At a moderate pressure reached during EMX detonation, it seems reasonable to neglect the compression of both glass and the matrix in the vicinity of the Chapman–Jouguet point in this formula. Then the value of α changes from 0.016 to 0.22 as μ varies from 3 to 50%.

The presence of non-conducting glass fragments can affect the measured electrical conductivity of the medium. To estimate this effect, we performed numerical simulations by the method described in [18]. The dependence of the electrical conductivity of the medium containing dielectric inclusions on the volume fraction of the dielectric can be presented as

$$\sigma_g/\sigma = 1 - 1.5\alpha,$$

where σ_g and σ are the electrical conductivities of the medium with non-conducting inclusions and the pure conducting component, respectively. This dependence is valid up to $\alpha = 0.5$. For the maximum value in our conditions $\mu = 50\%$ ($\alpha = 0.22$), the conductivity of the medium decreases approximately by one third.

The electrical conductivity values given below are corrected by this value to accentuate the role of the conducting phase. In the course of expansion of detonation products, the volume fraction of the dielectric α decreases and the blocking effect of inclusions becomes attenuated. It is difficult to take into account these changes within the framework of the present study; therefore, the coefficient of recalculation for the entire measured profile $\sigma(t)$ was assumed to be constant and corresponding to the assumption that the density of the conducting component is equal to the initial density of the matrix, as was mentioned above. Thus, the most precise correction corresponds to the vicinity of the reaction zone where the maximum (or close to that) electrical conductivity was observed and where the values of σ are close to the true electrical conductivity of the conducting component. This procedure ensures a more accurate comparison of different compositions. The shape of the profile, i.e., its relative changes, reflects the behavior of the directly measured electrical conductivity of the medium with inclusions σ_g; the electrical conductivity of the conducting phase decreases slightly faster during expansion of detonation products.

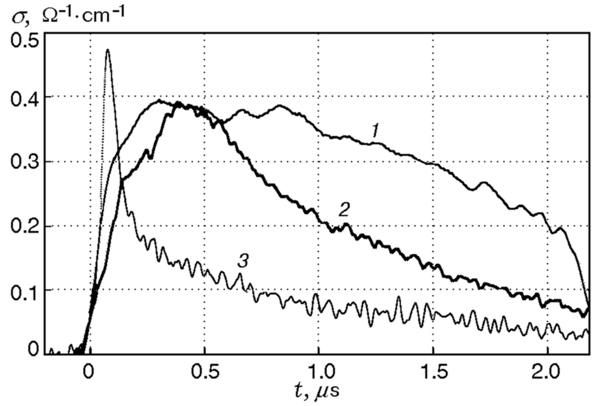

Fig. 2. Profiles of electrical conductivity in the case of AN/SN-emulsion-based EMX detonation at $\mu = 8$ (*1*), 40 (*2*), and 50% (*3*).

EXPERIMENTAL RESULTS AND DISCUSSION

The pressure, temperature, and density of the substance increase behind the detonation front. The composition of explosion products changes in the course of the chemical reaction; their thermal dissociation and ionization are possible. As a result, electrical conductivity appears behind the wave front.

AN/SN Emulsion

Figure 2 shows three typical profiles of $\sigma(t)$ for an EMX based on the AN/SN emulsion. The EMX parameters are varied within wide limits: density 1.2–0.5 g/cm^3, detonation velocity 5–2.1 km/s, and detonation pressure 8–0.7 GPa. The reaction time and the EP temperature change comparatively weakly in this range of pressure: 0.5–0.8 μs [9] and 1750–2100 K [19, 2].

The maximum value of the electrical conductivity $\sigma_{\max} \approx 0.4$–$0.5\ \Omega^{-1}\cdot\text{cm}^{-1}$ is reached during $t_{\max} \approx 0.1$–$0.5\ \mu$s. During the next 2 μs, the elec-

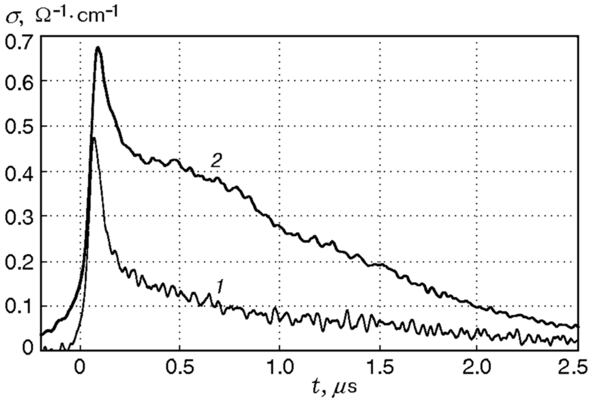

Fig. 3. Effect of the initiation power on the profile of $\sigma(t)$ for the AN/SN emulsion at $\mu = 50\%$: normal detonation (*1*) and overdriven detonation (*2*).

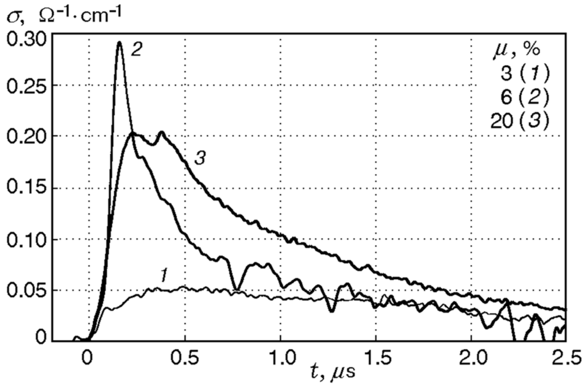

Fig. 4. Profiles of electrical conductivity in the case of AN-emulsion-based EMX detonation with different fractions of microspheres.

trical conductivity decreases, and this decrease is faster as the amount of glass microspheres increases.

The initial growth of electrical conductivity can be naturally related to the change in the state of the substance in the course of the chemical reaction. In particular, the "hot spots" formed mainly due to collapsing of microspheres start to burn more intensely and then coalesce with each other. Moreover, the reaction induces an overall increase in temperature and a change in the composition. The decrease in electrical conductivity after the reaction completion is apparently caused by the decrease in parameters within the Taylor wave.

The composition with $\mu = 50\%$ is the least powerful substance among all EMXs considered in this study; the initial volume fraction of the emulsion in this composition is approximately 25%. This composition is the most appropriate for obtaining overdriven detonation. When the mass of the initiating charge was changed, both normal detonation (curve *1* in Fig. 3; $D = 2130$ m/s) and overdriven detonation (curve *2*; $D = 3000$ m/s) could be obtained. The initiation intensity produces a minor effect on the duration of the peak of $\sigma(t)$, and $\sigma_{\max}$ increases by 30%. The electrical conductivity in the expansion wave in the next 2 μs is 2–3 times higher for curve *2* than for curve *1*, which is also apparently related to the higher temperature in the overdriven detonation wave.

AN Emulsion

Figure 4 shows three profiles of electrical conductivity for an AN-emulsion-based EMX. The detonation velocity changes from 4.0 to 3.5 km/s, and the pressure changes from 8.4 to 1.9 GPa. The nonmonotonic evolution of the profile of $\sigma(t)$ due to changes in μ should be noted. We should particularly mention the composition with $\mu = 6\%$ (curve *2*) which displays the maximum electrical conductivity $\sigma_{\max} \approx 0.3\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ and the greatest rate of its decrease. For certainty, we performed four experiments with this composition; qualitatively, the characteristics of the profile of $\sigma(t)$ remained unchanged, and the values of $\sigma_{\max}$ were in the interval 0.28–0.43 $\Omega^{-1}\cdot\mathrm{cm}^{-1}$. For this composition, the profile of $\sigma(t)$ is similar to curve *3* in Fig. 2, for which the number of sensitizing inclusions is greater almost by an order of magnitude ($\mu = 50\%$). The reason for this behavior of the AN-emulsion-based EMX with $\mu = 6\%$ is probably related to creation of optimal conditions for detonation, while deviation from these conditions ensures weaker ionization. An indirect confirmation of optimal conditions for this composition is the fact of reaching the minimum length of the chemical spike [9].

Effect of Pressure and Temperature

For the EMX based on the AN/SN emulsion, $\sigma_{\max}$ weakly depends on the detonation pressure p (Fig. 5). As the pressure changes by more than an order of magnitude, the value of $\sigma_{\max}$ changes approximately by a factor of 2.5, and a decrease in $\sigma_{\max}$ is observed at the maximum pressures. This situation differs from the behavior of $\sigma_{\max}$ for monomolecular explosives. For example, for RDX, $\sigma_{\max}$ is approximately proportional to the detonation pressure [12, 13] (points *3* in Fig. 5). The behavior of $\sigma_{\max}$ for the EMX is similar to the evolution of the calculated temperature of explosion products [19] (curve *4* in Fig. 5). It may be assumed that the maximum electrical conductivity for the AN/SN-emulsion-based EMX is mainly determined by the EP temperature.

For the purely AN-emulsion-based EMX, the dependence $\sigma_{\max}(p)$ is nonmonotonic, and the maximum

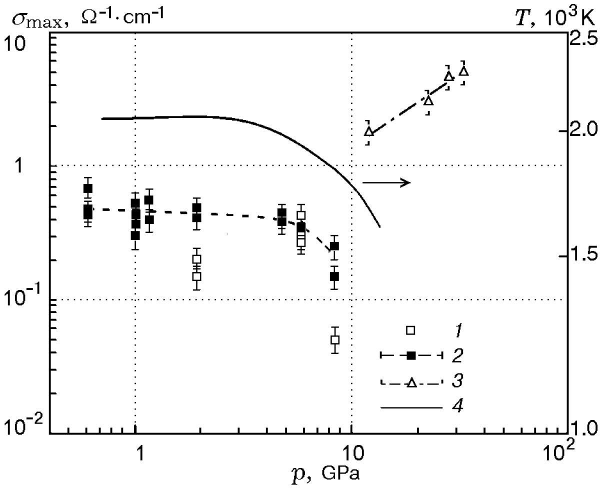

Fig. 5. Maximum electrical conductivity versus pressure: curves *1* and *2* show the results for the EMXs based on the AN emulsion and AN/SN emulsion, respectively, curve *3* shows the results for [12, 13], and curve *4* shows the EMX detonation temperature [19].

is reached in the case with addition of 6% of the sensitizer (cf. Fig. 4).

Effect of the Emulsion Composition

Figure 6 shows the data for emulsions of different compositions with $\mu = 3$ and 20%. Figure 6b also illustrates the repeatability of experiments. The common feature for all profiles of $\sigma(t)$ is a lower (by a factor of 2–3) value of electrical conductivity of explosion products for the AN-emulsion-based EMX as compared to the AN/SN-emulsion-based EMX. The thermodynamic parameters of these compositions obtained during the explosion are similar to each other because the content of sodium nitride is only ≈10%. In fact, a small part of one oxidizer (AN) is replaced by the other oxidizer. The growth of electrical conductivity due to addition of the $NaNO_3$ metal salt is obviously caused by charge carriers from sodium-containing reaction products.

Following [20], let us consider a possibility of electrolitic dissociation behind the detonation front favored by the presence of water, which is included into the initial EMX composition and is one of the main components of explosion products [7]. Naturally, dissociation is facilitated at the explosion temperature of ≈2000 K. The role of sodium agrees with this hypothesis if the Na^+ ion is formed easier than other possible candidates. Indeed, aqueous solutions of salts are good conductors even under room conditions. The contribution of sodium ions to electrical conductivity of EMX detonation products is comparatively large and reaches 0.1–0.2 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$.

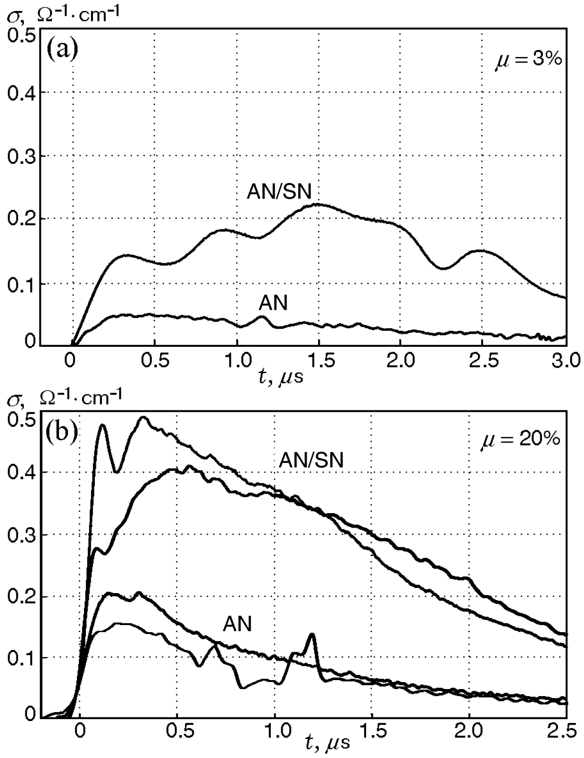

Fig. 6. Profiles of electrical conductivity in the case of EMX detonation.

The lower conductivity in the case of an explosion of the AN-emulsion-based EMX may be due to water dissociation into H^+ and OH^- ions, which is also stimulated by the high temperature of the explosion (as was mentioned above, shock pressure alone is insufficient for water dissociation). Thus, electrical conductivity behind the front of EMX detonation possibly has an ionic nature.

Correlation of Electrical Conductivity and Reaction Time

A typical feature of all previously studied monomolecular balanced high explosives (RDX, HMX, and PETN) is fast reaching of the maximum electrical conductivity, almost within the limits of resolution of the method. The duration of the electrical conductivity peaks is close to the chemical spike duration obtained by optical methods [13]. The maximum electrical conductivity monotonically increases with density (points *3* in Fig. 5).

Typical features of EMXs are lower values of the maximum electrical conductivity ≈0.4 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ and a weak dependence on density. The time needed to reach the maximum electrical conductivity varies from 0.1 μs at $\mu = 50\%$ to ≈0.5 μs at $\mu = 3\%$ and increases with increasing density and decreasing number of microspheres ("hot spots"). This behavior can be explained by the formation and condensation of a spatial grid of the conducting phase, which arises due to intensification of burning and coalescence of "hot spots."

As is seen from Figs. 2 and 4, the EMX electrical conductivity profiles sometimes display clearly expressed peaks on the background of quasi-equilibrium ion conductivity; the duration of these peaks may correlate with the reaction time. In the reaction (chemical spike) zone, the increase in electrical conductivity can be induced by the increase in both pressure and temperature. The chemical reaction includes the formation of nonequilibrium intermediate products, which may contribute to electrical conductivity.

For the EMX based on the AN/SN emulsion, a clear peak of electrical conductivity is observed only at $\mu = 50\%$, and its duration is 0.2 μs. At the same time, the duration of the peak on the velocity profile of the EMX/PMMA interface obtained in [9] is 0.6 μs. The difference is possibly caused by using different methods for studying the detonation front structure. Thus, the duration of the peak of $\sigma(t)$ can be considered as an estimate of the reaction time at $\mu = 50\%$. At smaller values of μ, the decrease in the electrical conductivity profile is much slower. Apparently, the slowly decreasing quasi-equilibrium ion conductivity in such compositions disguises the reaction zone, and the method of electrical conductivity does not allow its identification. In a low-density composition with $\mu = 50\%$, the contribution of ion conductivity is smaller, and the peak electrical conductivity seems to be related to proceeding of the chemical reaction.

For the EMX based on the AN emulsion, clearly expressed peaks of electrical conductivity are obtained at $\mu = 6$ and 20%. Their durations are approximately 0.4 and 0.6 μs, respectively, which is fairly close to the data obtained by the optical method. At $\mu = 3\%$, the peak is not obtained, and the conductivity seems to have a quasi-equilibrium character.

CONCLUSIONS

The characteristic values of the maximum electrical conductivity of explosion products of emulsion explosives based on aqueous solutions of ammonium and sodium nitrides are 0.4–0.5 $\Omega^{-1} \cdot \text{cm}^{-1}$, weakly depend on the detonation pressure, and correlate with the estimates of the EP temperature.

The presence of a small amount of sodium nitride in the oxidizer increases the conductivity by a factor of 2–3 as compared to the emulsion containing ammonium nitride only. The reason is the formation of additional charge carriers during metal salt decomposition. The presumed mechanism of conductivity of the EMX based on the AN/SN emulsion is electrolitic dissociation in detonation products, which can be actually considered as a dense hot solution of an electrolyte. The rate of conductivity reduction in the rear expansion wave is largely determined by the concentration of the physical sensitizer (hollow glass microspheres).

It turned out that it is more difficult to interpret the electrical conductivity profiles obtained in this work than in the case of balanced molecular explosives, which is natural because of a more complicated structure of EMXs. Nevertheless, the high-resolution method of measuring the electrical conductivity turned out to be useful for studying detonation of heterogeneous emulsion-based compositions, and new information was obtained in addition to that found by using traditional methods.

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