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Measuring the voltage-current characteristic of pentaerythritol tetranitrate and trinitrotoluene composites containing single-walled carbon nanotubes

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Abstract. This paper provides results of measuring the conductivity of explosives pentaerythritol tetranitrate and trinitrotoluene composites containing single-walled carbon nanotubes. The conductivity depends on the applied voltage nonlinearity and irreversibly changes under the influence of current loads about several amperes for milliseconds.

1. Introduction
Presently, single-walled carbon nanotubes (SWCNT) are applied to modify various properties of different materials. One of the most important properties of composites containing carbon nanotubes is high electrical conductivity. The addition of small quantities (less than 1%) of SWCNT provides high conductivity for initially nonconductive materials. A rich experience in both production and applying composites with CNT has been already accumulated. [1].

The phenomenon of conductivity of such composites is described by percolation mechanism: the ends of tubes touch each other inside the dielectric, so the conductive chains are formed within the volume of the sample [1]. The conductivity is determined by the concentration and homogeneity of mixing SWCNT, but achieving a homogeneous distribution is a complex technological issue.

This research is focused on studying the conductive properties of composites based on high explosives: (HE) pentaerythritol tetranitrate (PETN) and trinitrotoluene (TNT) with the content of SWCNTs in the mass fraction of 0.5%. The samples were produced by the method described in article [2]: the solution of HEs in acetone was poured in aqueous suspension of SWCNT. The molecules of HEs were deposited on SWCNT as a grey precipitate. The remaining liquid became clear. The resulting precipitate was compressed into the desired shape. Composites based on HEs have comparable conductivity to other polymer composites [1] at similar values of SWCNTs concentration.

2. Measurement procedure
Prolonged exposure to the current has risk of causing the detonation of the HE sample. Therefore, only a very short application of an impulse voltage to the sample is advisable to avoid detonation during measurement. A scheme was chosen with the discharge of the capacitor. Inductance is necessary to suppress the effects of self-inductance of wires and samples. Figure 1 shows the schematic diagram of the setup used to measure conductivity.
The cylindrical samples of HE with SWCNTs are placed between two copper electrodes (Fig. 2). A series of experiments with distinct initial voltage of a capacitor has been performed. Parameters of samples are shown in Table 1.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Height, cm</th>
<th>Diameter, cm</th>
<th>Mass, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNT</td>
<td>1.84</td>
<td>1.96</td>
<td>7.33</td>
</tr>
<tr>
<td>PETN</td>
<td>1.85</td>
<td>1.96</td>
<td>7.75</td>
</tr>
</tbody>
</table>

3. Results
Figure 3 is a view of oscillogram for TNT. Other oscillograms have similar view.

Figure 4 shows the dependence of the TNT sample resistance on the applied voltage. This graph corresponds to the voltage on the capacitor in 15 V. Resistance values at the same voltage differ. The upper line corresponds to an increase in voltage, and the lower line is a decrease in voltage. Presumably, this is due to the dependence of the SWCNT resistance on temperature. Under the assumption of a percolation conduction mechanism, the conductor in the sample is UNT chains, providing strong localization of the sample for its heating during the experiment.
The article [3] presents the experimental results of CNT film conductivity measurement. The resistance of the film was inversely proportional to the square root of the temperature from 0.03 to 300 K. The article [4] provides the proportionality of the resistance of an individual single-walled nanotube of metal type as $T^{-0.6}$, and for an individual single-wall semiconductor as $T^{-3.9}$. Based on this, we can estimate the proportion of CNTS that participate in the percolation conduction mechanism. We assume that during the experiment the heat does not have time to transfer from nanotubes to the surrounding substance. Specific heat $c$ is estimated at about 700 J/(kg*K)[5]. We take $R_0 = 5$ Ohm, $R_T = 4$ Ohm, and $T_0 = 300$ K. Hence, SWCNT were heated approximately to 20 K. The estimation of the amount of conducting CNTS on the basis of the temperature dependence of metal nanotubes gives the heating value of approximately 100-150 °C.

The amount of energy released can be measured by considering figure 3. We estimate average voltage $U \approx 7.5$ V, average current $I \approx 1$ A, and duration as 1 ms. Then the released energy $Q$ is approximately equal to 0.02 J. The number of conductive nanotubes $m = q/c \Delta T \approx 0.3 - 1.4 \times 10^{-3}$ g. Mass of all SWNT in PENT sample equals to 0.038 g. The share of conductive CNTS is about 0.5-4% of all nanotubes in the sample, or about 0.001% in the mass fraction. For TNT, the estimate gives a similar result. This estimate is consistent with data on percolation conductivity in [1], where minimal percolation threshold was about 0.003%, and depended on the method of mixing.

Figures 5, 6 show the resistance-voltage dependences of samples of TNT and PETN. On both graphs, the upper part corresponds to the voltage increase on the samples, respectively, and the lower part of the line – voltage drop. The characteristic resistance values falls from experiment to experiment for both samples. At the same time, the resistance values for both samples are quite similar with almost the same geometry and mass fraction of samples.

The conductivity of the PETN sample showed a sharp rise when a capacitor voltage was 35 V (Fig. 7). The lower line is the voltage increase, and the upper line is its decrease. When the voltage rose by about 20 V the resistance began to increase, and with further changes in the voltage it began to rise to the value of 10 Ohms. The following experiments showed that the characteristic values of resistance of the PENT sample began to change in the range from 20 to 40 Ohms, and resistance began to change: the values of resistance during decreasing the voltage were less than during its increasing. (Fig. 8). Presumably, this was caused by strong thermal heating of conductive tubes under prolonged exposure of current loads. Probably it could change the internal structure of the substance. Taking into account the heating rate for CNTs with metal conductivity of the order of 100-150 °C, the melting point of 141.3 °C and the decomposition temperature of 150 °C, this could change the internal
microstructure of the PETN composite. A similar behavior for TNT of the conductivity was not observed for the used voltage range.

After experiments on successive increase of charging voltage on the capacitor, measurements for initial values of voltage on the capacitor were again carried out. Figures 9, 10 presents the results of comparison at low starting voltage on the capacitor.

4. Conclusions
The paper presents experimental measurements of the conductivity of the sample explosive of PETN and TNT with a mass fraction of CNTS of 0.5% in the range up to 40 V. The obtained values of conductivity comparable to the conductivity values of other polymer composites with similar concentrations of SWCNT.

The dependence of conductivity on the applied voltage was observed. Moreover, the resistance values were different at the same voltage values: when the voltage on the sample decreased, the resistance had lower values. This effect can be caused by thermal effect: the resistance of SWCNT is inversely proportional to temperature. An appropriate assessment was carried out, revealing that the mass of the conducting nanotubes was less than the mass of all the tubes in the samples.
For both samples, the effect of irreversible change in conductivity was observed. The range of characteristic values of resistance decreased from experiment to experiment. For both samples characteristic values of resistance decreased.

When voltage on the PETN’s sample was about 20 V conductivity increased sharply. The current was about 2 A and the flow time was about 1 millisecond. As a result, the characteristic values of the resistance increased about 4-6 times. This could be caused by the strong heating of the CNT and the surrounding matrix of the substance, but the assumption requires additional research. The TNT sample had no similar behavior in the used voltage range.

References