Influence of some additives on burning rate of KNO$_3$-based compositions

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Abstract. In this article effect of some additives on combustion behaviour of high energetic compositions based on KNO$_3$ was studied. The KNO$_3$-based samples were made by mixing, rolling, and pressing. Investigated additives were: copper salicylate, nickel salicylate, copper-lead phthalate, nickel-lead phthalate, soot and carbon nanotubes. Burning rate was determined by the pressure increasing by using modification of the corner point method. It is shown that individual additives insignificantly effect on the burning rate of studied samples. The carbon nanotubes brand TMD with specific surface area $\sim$270 m$^2$/g and copper salicylate are the most effective additives on the burning rate. It should be noted that copper salicylate with carbon nanotubes have a significantly greater effect on the burning rate than individual additives or the catalyst with soot.

Keywords: KNO$_3$, catalyst, carbon nanotubes, burning rate.

Classification numbers: 2.6.1, 2.9.4.

1. INTRODUCTION

Potassium nitrate (KNO$_3$) is a very important and common oxidizing agent for the manufacture of high energetic compositions. KNO$_3$ is used to produce black powder, which is widely used in firearms, artillery, rockets and fireworks, as well as fuses [1 - 3]. The black powder contains up to 75-weight percent (wt.%) KNO$_3$ and is the first igniter composition. In dim igniter compositions for tracers, KNO$_3$ is the main component [4 - 6]. For example, modern igniter compositions (universal) contain up to 50 - 75 % KNO$_3$, 6 - 30 % metal (Al, Mg, Ti) and 2 - 9 % binder. Thermite incendiary compositions contain up to 66 % KNO$_3$ and 19 % metal [7 - 10]. When KNO$_3$ is introduced into thermitite, its thermal effect increases, a flame is formed during combustion and the flash point decreases, but the sensitivity of the composition to mechanical stress increases.

In the production of masking fumes, KNO$_3$ is used as one of many oxidizers for sublimation type formulations that produce stable, low toxicity fumes and mists when burned. Various versions of these compositions can contain up to 20 - 30 % KNO$_3$ [11 - 14]. KNO$_3$ was
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also used as an additional oxidizing agent for the production of shock and spike compounds. Compositions of this type contain up to 60% KNO₃, up to 60% initiating explosive (stypbate, lead azide, lead picrate, etc.), 5-55% fuel (antimony sulfide, calcium silicide, etc.), up to 15% sensitizer, up to 50% inert sensitizer (glass, carborundum), up to 15% blowing agent (heating element, trinitrotoluene...) and 0.1-6% binder [15]. To obtain pyrotechnic spark-force compositions [16], KNO₃ was used as an additional oxidizing agent (9-21%) in order to increase the functional reliability and expand the spark-force effect. In the exothermic composition for heating devices, KNO₃ is used as an additional oxidizing agent with a content of 3 to 10% [17]. KNO₃ plays an important role in aerosol-forming fire extinguishing compositions [1, 3, 7-9].

Obviously, KNO₃ is widely used as part of compositions for various purposes. To create highly efficient energy-rich KNO₃-based compositions for various purposes, it is necessary to have the ability to control the burning rate, its dependence on pressure in a different pressure range. This is usually accomplished by introducing combustion catalysts into the formulations of compositions. For double base propellants, the most effective of additives are combined catalysts, consisting of various transition metal salts, in combination with soot.

The aim of this work was to study the effect of some catalysts and carbon materials on the burning rate of the compositions.

2. MATERIALS AND METHODS

2.1. Materials

Compositions based on phenolformaldehyde resin (2÷3% free phenol) and KNO₃ - 99% purity, were studied. Phenolformaldehyde resin was plasticized dibutyl phthalate with a ratio phenolformaldehyde resin/dibutyl phthalate = 3:2.

To improve the physico-mechanical and technological characteristics, 1.5% teflon and 0.5% calcium stearate were introduced into the samples. The modified additives were produced by company LLC “Formoplast”.

Copper salicylate (SalCu-C₇H₆O₆Cu₂) - green powdery substance with particle size ≤ 5 µm, nickel salicylate - C₇H₆O₆Ni₂ with particle size ≤ 1 µm, copper-lead phthalate - C₈H₈CuO₃Pb - fine powder of turquoise or green color with particle size ≤ 5 µm and nickel-lead phthalate - C₈H₆O₃Ni₂Pb - were used as catalysts.

Soot brand UM-76 with specific surface area ~170 m²/g was supplied by company CJSC “KhimPlast”. Carbon nanotubes (CNTs) - filamentary and nanoscale formations of polycrystalline graphite of cylindrical shape with an outer diameter of 10 - 30 nm, an inner diameter of 5 - 15 nm, specific surface area ≥ 270 m²/g, a TM brand length of ≥ 2 µm, and TMD brand length of ≥ 20 µm - were supplied by company Zavkom JSC.

The purity of the additives was more than 99%.

2.2. Methods

2.2.1. Mixture of components

To study the dependence of the burning rate of the samples on the pressure, particle size of oxidizer 90 - 160 µm was used. The components were pre-dried and mixed with resin and technological additives, then the plasticizer was added to the mixture. The obtained mass was
thoroughly mixed to the paste state, then it was rolled at a certain inter-roll gap.

2.2.2. Rolling of paste

The samples were made by using rolling with a roll gap of 0.6 mm. Rolling was carried out on rollers, consisting of a roller apparatus. The mixture was rolled in the mode of movement of the rolls towards each other. At the beginning, it is necessary to set a certain gap depending on the dispersion of the components and the minimum speed of the rolls for the formation of flat rectangular plate. At the end, the speed of the rolls was increased to ~ 10 and the flat rectangular plate was run 25 times in order to form a structural grids and homogenization.

2.2.3. Pressing of sample

Pressing cords from the obtained flat rectangular plate was carried out on a universal tensile machine ZD 10/90 (press). The press allows to develop loads up to 10 tons, has 6 indicator ranges with different measurement accuracy, is equipped with a speed change regulator from 0.05 to 100 mm/min and a diameter of d ~ 7 mm.

2.2.4. Method for determining the burning rate of samples in a constant pressure bomb

The experiment was carried out on cylindrical (without a channel) gunpowder charges with a diameter of ~ 7 mm and a given height h ~ 15 mm. The combustion process of the sample is fixed in the form of an oscillogram P = f(τ), on which 2 corner points are visible: the first corresponds to the beginning of the charge burning, the second - to the end of combustion (Figure 1). Knowing the length of the burnt sample, the average burning rate at medium pressure is calculated [18].

Figure 1. A typical oscillogram of the dependence of pressure on the burning time of the samples.

The dependence of the burning rate \( r_b \) of the samples on the pressure \( p \) was expressed by the following combustion formula. The burning rate determination accuracy was ± 2 %.

\[
r_b = a.p^n
\]

where: \( a \) and \( n \) are coefficients depended on ingredients and ratio of them.
3. RESULTS AND DISCUSSION

It is necessary to note that the various binders were used for studying the behavior of combustion of systems based on KNO₃ with other binders (for example: nitrile butadiene rubber, polyvinyl butyral) without additives and determined that the obtained samples do not burn at low pressures from 0.1 to 4 MPa. Such data were also obtained for compositions based on KNO₃ with nitrocellulose. These samples begin to burn only when soot, catalyst or phenolformaldehyde resin are added. The phenolformaldehyde resin is a cheap polymer, and the choice of this binder is due to the fact that highly efficient aerosol-forming fire extinguishing compositions. The charges from which are obtained using rolling and continuous pressing and have high mechanical characteristics and a density close to the calculated one [19]. It ensures combustion layer-by-layer of the charges in a wide pressure range.

It is known that many of energy materials do not burn at atmospheric pressure or burn at a low rate [20 - 23]. For example, double base propellants, even with a high content of nitroglycerine (to 50 - 70 %), burn at a speed of 0.9 - 1.2 mm/s; gunpowder based on diethylene glycol dinitrate does not burn. In our previous work KNO₃-based compositions with oxidizer excess coefficient (α) have an increased ability to burn at atmospheric pressure [20, 21]. For most studied KNO₃-based samples in [20], the dependence of burning rate on pressure consists of two sections: in the first section, the value of n is 0.06 - 0.28, and in the second section, the value of n is much higher: 0.47 - 1.56. The dependence of rb on α has an extremal character: the maximum burning rate (rbmax) is found at the coefficient α ~ 0.72 (Figure 2).

![Figure 2. Dependence of the burning rate of samples on the value of α](image)

1- at 0.1 MPa; 2- at 4 MPa; 3- at 10 MPa; 4- at 18 MPa.

By above results, the KNO₃-based samples with coefficient α ~ 0.72 and 1 were chosen for effect study of additives on combustion behaviour. The influence of additives on the burning rate of the systems was evaluated by the value Z = rb-add/rb-0, where rb-add and rb-0 are the burning rates of the sample with and without the additives, respectively.

3.1. Influence of 2 % catalysts on the burning rate of the sample with coefficient α ~ 1

The effect of catalysts on the burning rate of sample with the coefficient α ~ 1, which burns slowly (rb-0,1 ~ 1.2 mm/s), was studied. Individual catalysts were introduced into the sample in an amount of 2 % (over 100 %).
As shown in Figure 3 and Table 1, it can be seen that nickel salicylate has almost no effect on the combustion of the basic sample. Nickel-lead phthalate increases the burning rate relatively weakly. SalCu and copper-lead phthalate have a significant effect on the burning rate: at 0.1 MPa, the Z value is 2.1 and 2.0, respectively.

**Figure 3.** Effect of 2 % catalysts on the burning rate of a sample based on KNO₃:
1- without additives α ~ 1; 2- nickel salicylate; 3- nickel-lead phthalate; 4- copper-lead phthalate; 5- SalCu.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>a</th>
<th>n</th>
<th>ΔP, MPa</th>
<th>$r_b$ 0.1- mm/s</th>
<th>$r_b$ 0.4- mm/s</th>
<th>$r_b$ 10- mm/s</th>
<th>$Z_{0.1}$</th>
<th>$Z_{0.4}$</th>
<th>$Z_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>2.39</td>
<td>0.28</td>
<td>0.1 - 4.2</td>
<td>1.2</td>
<td>-</td>
<td>3.4</td>
<td>-</td>
<td>8.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.76</td>
<td>1.05</td>
<td>4.2 - 18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 % SalCu</td>
<td>5.2</td>
<td>0.32</td>
<td>0.1 - 0.7</td>
<td>2.5</td>
<td>2.1</td>
<td>8.2</td>
<td>2.3</td>
<td>13.4</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>4.55</td>
<td>0.47</td>
<td>4.0 - 18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 % nickel</td>
<td>2.43</td>
<td>0.27</td>
<td>0.1 - 4.0</td>
<td>1.3</td>
<td>1.1</td>
<td>3.6</td>
<td>1.0</td>
<td>8.8</td>
<td>1.0</td>
</tr>
<tr>
<td>salicylate</td>
<td>0.90</td>
<td>0.99</td>
<td>4.0 - 18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 % copper-lead</td>
<td>4.90</td>
<td>0.29</td>
<td>0.1 - 2.0</td>
<td>2.4</td>
<td>2.0</td>
<td>7.3</td>
<td>2.1</td>
<td>12.2</td>
<td>1.4</td>
</tr>
<tr>
<td>phthalate</td>
<td>3.43</td>
<td>0.55</td>
<td>2.0 - 18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 % nickel-lead</td>
<td>3.18</td>
<td>0.32</td>
<td>0.1 - 6.0</td>
<td>1.5</td>
<td>1.3</td>
<td>5.0</td>
<td>1.4</td>
<td>8.9</td>
<td>1.0</td>
</tr>
<tr>
<td>phthalate</td>
<td>1.12</td>
<td>0.90</td>
<td>6.0 - 18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalysts do not change the nature of the dependence of the burning rate on pressure, on which there are two sections: the value of n (0.11 - 0.32) in the first section is much lower than in the second section (0.47 - 0.99). With an increase in pressure (up to 4 MPa), the value of Z increases to a maximum, then drops. It has been established that the most effective catalyst for the burning rate of the sample is SalCu: at 4 MPa, $Z_{\text{SalCu}} = 2.3$.

### 3.2. Effect of soot and CNTs on the combustion of the sample with coefficient α ~ 0.72

Effect of soot and CNTs was carried out for the fast-burning sample with α ~ 0.72, which
greatly burns faster than the sample with \( \alpha \sim 1 \). The soot and CNTs were introduced into the sample in an amount of 2\% (over 100\%).

![Graph showing burning rate vs pressure](image)

*Figure 4. Effect of 2\% soot and CNTs on the burning rate of sample based on KNO\(_3\):*

1- without additives (\( \alpha \sim 0.72 \)); 2- UM-76; 3- TM; 4- TMD.

*Table 2. Effect of soot and CNTs on the combustion of the sample with coefficient \( \alpha \sim 0.72 \).*

<table>
<thead>
<tr>
<th>Additive</th>
<th>( a )</th>
<th>( n )</th>
<th>( \Delta P ), MPa</th>
<th>( r_b^{0.1}), mm/s</th>
<th>( Z_{0.1} )</th>
<th>( r_b^{4}), mm/s</th>
<th>( Z_{4} )</th>
<th>( r_b^{10}), mm/s</th>
<th>( Z_{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %</td>
<td>7.45</td>
<td>0.16</td>
<td>0.1 - 4.1</td>
<td>5.0</td>
<td>-</td>
<td>9.3</td>
<td>-</td>
<td>14.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.74</td>
<td>0.48</td>
<td>4.1 - 18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 % UM-76</td>
<td>9.94</td>
<td>0.22</td>
<td>0.1 - 18</td>
<td>6.2</td>
<td>1.2</td>
<td>13.5</td>
<td>1.5</td>
<td>16.5</td>
<td>1.2</td>
</tr>
<tr>
<td>2 % TM</td>
<td>11.84</td>
<td>0.23</td>
<td>0.1 - 18</td>
<td>7.0</td>
<td>1.4</td>
<td>16.3</td>
<td>1.7</td>
<td>20.2</td>
<td>1.4</td>
</tr>
<tr>
<td>2 % TMD</td>
<td>12.96</td>
<td>0.25</td>
<td>0.1 - 18</td>
<td>7.3</td>
<td>1.5</td>
<td>18.3</td>
<td>1.9</td>
<td>23.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The soot and CNTs increase the burning rate of the sample in a wide pressure range and the dependence of \( Z \) on pressure has an extreme character at 4 MPa. This probably is explained by the same reason for the acceleration of combustion. In contrast to the initial sample, the burning rate of samples with additives unambiguously depends on pressure. At the same time, the \( n \) value of these samples is almost the same: 0.22 - 0.25 (Figure 4, Table 2) and is close to the \( n \) value of the original sample in the first section. A strong drop in the value of \( Z \) above 4 MPa is due to the fact that the value of \( n \) for the basic sample after 4 MPa increases by \( \sim 3 \) times, and for samples with additives remains constant. Especially, the CNTs have a stronger effect on the burning rate of the sample than soot. This may be due to higher thermal conductivity and higher reactivity of CNTs when interacting with the condensed phase nitrate melt.

### 3.3. Effect of soot and CNTs on the catalytic combustion of sample with coefficient \( \alpha \sim 0.72 \) at atmospheric pressure

The fast-burning sample (\( \alpha \sim 0.72 \)) with SalCu, UM-76 and TMD were studied. The individual additives and their mixtures were introduced into the sample with an amount of 2\% (over 100\%). Individually, 2\% SalCu and 2\% TMD accelerate the burning rate of the sample.
Soot accelerates the combustion of basic samples to a weaker extent than the CNTs.

![Figure 5](image)

Figure 5. Effect of soot and CNTs on the catalysis of combustion of the sample at atmospheric pressure.

The effectiveness of combined additives SalCu with UM-76 or TMD on burning rate depends on the ratio of SalCu with UM-76 or TMD in the sample. The Z curve has an extreme character: $Z_{\text{max}} \sim 1.7$ at a ratio of SalCu with UM-76 (or TMD) $\sim 1:1$, i.e. soot and CNTs slightly increase the effect of the catalyst (for 2% individual SalCu $Z_{\text{max}} \sim 1.5$).

### 3.4. Effect of the soot and CNTs on the catalytic combustion of sample with coefficient $\alpha \sim 0.72$

It was already noted in 3.3 that the soot and CNTs were introduced at atmospheric pressure by reducing the amount of SalCu. In this case, the soot only slightly increases the efficiency of the catalyst, and CNTs increase the efficiency of SalCu more strongly, but the CNTs sample (2%) are affected more than the combined addition 1% SalCu + 1% CNT and 2% SalCu. In next series of experiments, the effect of combined catalyst containing a constant amount (2%) of SalCu and different amount of carbon additives (over 100%) was investigated (Table 3 and Figure 6).

It can be seen that the 2% SalCu + 1% UM-76 and 2% SalCu + 2% UM-76 have approximately the same effect on the combustion behaviour of the studied sample ($Z_{0.1} = 1.5 - 1.6$ and $Z_{10} = 1.4 - 1.5$). These results are similar to that of the sample with 2% SalCu without the soot. This means that soot has little effect on the efficiency of SalCu. The SalCu with CNTs TMD brand have a greater effect on burning rate of the sample than the catalyst without the CNTs. Similar results were observed for double base propellants [24 - 27] and for propellants based on NH$_4$NO$_3$ [28], when CNTs have the ability to increase the efficiency of the combustion catalyst better than soot. This can be explained as follows: role of the soot is to form a carbon frame on the combustion surface. The carbon frame is combustible component, whose oxidation by nitric oxide is catalyzed by catalysts. However, CNTs have a high thermal conductivity greater than soot, and a developed structure [29]. So, when the combustion of compositions containing CNTs occurs, a higher carbon frame is formed on combustion surface and covering a larger burning surface area, on which catalyst particles accumulated (much more than in the case of soot [24, 25]). This increases the effective surface area of the catalyst particles, where intense heat is generated, leading to an increase burning rate.
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Figure 6. Effect of additives on the burning rate of sample based on KNO₃ with α=0.72:
1- without additives; 2- 2 % SalCu; 3- 2 % SalCu+1 % UM-76; 4- 2 % SalCu + 2 % UM-76;
5- 2 % SalCu + 1 % TMD; 6- 2 % SalCu + 2 % TMD; 7- 2 % SalCu.

Table 3. The effect of additives on the combustion of the sample.

<table>
<thead>
<tr>
<th>Additive</th>
<th>a</th>
<th>n</th>
<th>ΔP, MPa</th>
<th>r_b 0.1, mm/s</th>
<th>Z₀.₁</th>
<th>r_b 4, mm/s</th>
<th>Z₄</th>
<th>r_b 10, mm/s</th>
<th>Z₁₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>7.45</td>
<td>0.16</td>
<td>0.1-4.1</td>
<td>5.0</td>
<td>-</td>
<td>9.3</td>
<td>-</td>
<td>14.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4.74</td>
<td>0.48</td>
<td>4.1-18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% SalCu</td>
<td>12.75</td>
<td>0.22</td>
<td>0.1-18</td>
<td>7.5</td>
<td>1.5</td>
<td>17.3</td>
<td>1.9</td>
<td>21.2</td>
<td>1.5</td>
</tr>
<tr>
<td>2% SalCu+ 1% UM-76</td>
<td>12.86</td>
<td>0.22</td>
<td>0.1-18</td>
<td>7.7</td>
<td>1.5</td>
<td>17.4</td>
<td>1.9</td>
<td>21.3</td>
<td>1.5</td>
</tr>
<tr>
<td>2% SalCu+ 2% UM-76</td>
<td>13.35</td>
<td>0.21</td>
<td>0.1-18</td>
<td>8.2</td>
<td>1.6</td>
<td>17.9</td>
<td>1.9</td>
<td>21.7</td>
<td>1.5</td>
</tr>
<tr>
<td>2% SalCu+ 1% TMD</td>
<td>14.39</td>
<td>0.21</td>
<td>0.1-18</td>
<td>8.5</td>
<td>1.8</td>
<td>19.3</td>
<td>2.1</td>
<td>23.3</td>
<td>1.6</td>
</tr>
<tr>
<td>2% SalCu+ 2% TMD</td>
<td>15.71</td>
<td>0.21</td>
<td>0.1-18</td>
<td>9.2</td>
<td>1.9</td>
<td>21.0</td>
<td>2.3</td>
<td>25.5</td>
<td>1.8</td>
</tr>
<tr>
<td>4% SalCu</td>
<td>15.16</td>
<td>0.22</td>
<td>0.1-18</td>
<td>9.1</td>
<td>1.9</td>
<td>20.6</td>
<td>2.2</td>
<td>25.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Indeed, when the catalyst is increased to 4 %, Z is the same as the Z value for the combined additive (2 % SalCu + 2 % TMD).

The dependence r_b(p) of catalyzed samples has only one section, as well as the samples with the soot and CNTs: the value of n is 0.21 - 0.22, it is slightly higher than that of the basic sample without catalyst (n = 0.16 in the first section). At a pressure above 4 MPa for the original sample, n increases to 0.48, i.e. the burning rate increases much higher than for the catalyzed samples, whose the n value is 2.2 times lower, which leads to a sharp drop in the Z value.

4. CONCLUSIONS

It has been established that the copper salicylate and CNTs brand TMD are the most effective additives for the burning rate of KNO₃-based compositions. The soot has little effect on the efficiency of the catalyst on burning rate of the samples. The CNTs allow to expand the regulation possibilities of the combustion behaviour of KNO₃-based compositions. The increase of the burning rate of CNTs is associated with the formation on the surface combustion of a
developed carbon frame, on which intense heat release. So, a bigger amount of heat is transferred from the gas phase to the condensed phase by conduction than soot. The copper salicylate in combination with CNTs has a significantly greater effect on the burning rate than individual catalyst, CNTs and soot. This is due to the accumulation of catalyst particles on carbon frame on combustion surface.

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CRediT authorship contribution statement. Nguyen Duy Tuan: Methodology, Investigation, Data analysis, Writing manuscript. Denhisuk A.P.: Data analysis, Supervision, Writing manuscript. Doan Minh Khai: Data analysis, Manuscript editing and discussion. Sizov V.A.: Manuscript editing and discussion, Supervision.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

7. Melnikov V. E. - Modern pyrotechnics, Moscow, 2014 (in Russian)