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Mechanical and Thermal Sensitivity of Mixtures of Ammonium Nitrate with Combustible Hydrocarbons

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Abstract—Two explosive compositions ISU-4K and ISU-5R based on ammonium nitrate with added coke, diesel fuel, and rubber crumbs are tested so as to establish their sensitivity to mechanical and thermal perturbations. The flash point corresponding to 60-s delay is established. The kinetic parameters of thermal disintegration of the explosives are determined. The information obtained may be used in compiling standard documents (of GOST, OST, TU, VTU, and other types) and writing industrial regulations.

Keywords: explosives, ammonium nitrate, coke fines, rubber crumbs, thermal analysis, flash point, activation energy, impact sensitivity, shear sensitivity

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In improving the effectiveness and safety of explosives in open-pit mining, a key trend is the expanded use of simple industrial explosives based on ammonium nitrate. In comparison with traditional explosives, they are less expensive and safer to produce and also lower in environmental impact.

The main deficiencies of such explosives are insufficient physical stability when uniform ammonium nitrate is employed; relatively low heat of combustion; and relatively low stability in the presence of water. These flaws may be attributed to the properties of the main components: ammonium nitrate and liquid explosive. To improve the stability, the energy characteristics, and the water resistance, we consider three-component mixtures based on combustible additives such as coal fines, wood shavings, and soot.

This approach is a response to economic and safety considerations and also to rising environmental requirements and interest in recycled materials (such as worn tires, coal dust, and coke fines). The solid combustible additive must be able not only to absorb any liquid fuel that is not retained by the ammonium-nitrate granules but also to ensure safe handling of the explosive.

In the present work, we continue the research in [1]. Attention focuses on the sensitivity of ISU-4K and ISU-5R explosive mixtures based on ammonium nitrate, which were developed at Mel'nikov Research Institute of Integrated Mineral Development, Russian Academy of Sciences. Table 1 presents their composition. These mixtures are physically stable but sensitive to mechanical perturbations.

Differential scanning calorimetry provides an overall picture of the behavior of the mixtures on heating. This method also permits comparison of the mixtures with pure ammonium nitrate and assessment of the influence of the added hydrocarbons on the thermal characteristics. We use a NETZSCH STA 449 F3 Jupiter instrument for synchronous thermogravimetric analysis and differential scanning calorimetry. For each composition, we record four thermograms, at

Table 1. Content of components in the ISU-4K and ISU-5R mixtures

Component	Content, wt %;	
	ISU-4K	ISU-5R
Granulated ammonium nitrate	86.0 ± 0.5	93.5 ± 0.5
Crushed ammonium nitrate	2.5 ± 0.5	2.0 ± 0.5
Diesel fuel	4.5 ± 0.5	2.25 ± 0.5
Coke fines	7.0 ± 0.5	–
Rubber crumbs	–	2.25 ± 0.5

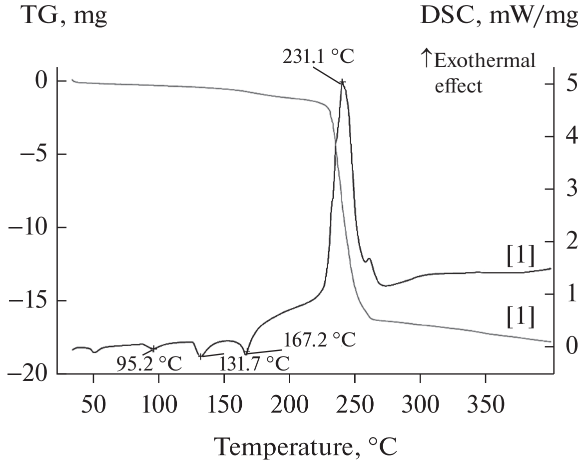

Fig. 1. Thermogram of ISU-4K explosive mixture (heating rate 5°C/min).

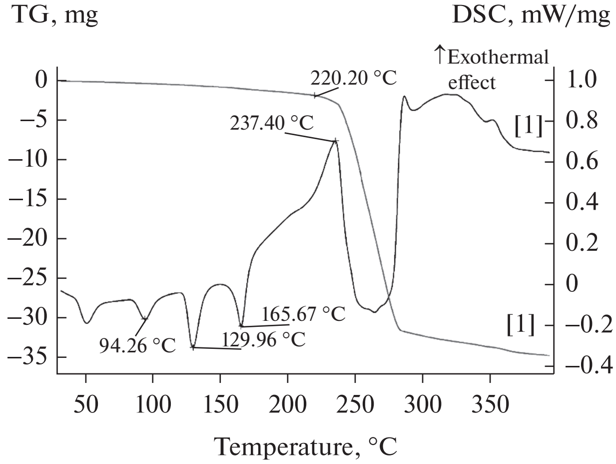

Fig. 2. Thermogram of ISU-5R explosive mixture (heating rate 5°C/min).

heating rates of 2.5, 5.0, 10.0, and 20.0°C/min. In Figs. 1 and 2, we show typical thermograms for the ISU-4K and ISU-5R mixtures, respectively. Table 2 presents data obtained by analysis of the thermograms for the mixtures and also pure ammonium nitrate.

It is evident from Table 2 that the thermograms of the ISU-4K and ISU-5R mixtures include four endothermal peaks, corresponding to phase transitions of pure ammonium nitrate (55, 93, 129, and 164°C). The phase-transition temperatures are consistent with the data for a heating rate of 2°C/min in [2]: 52.5, 89.0, 127.0, and 169.0°C. With increase in heating rate, the exothermal and endothermal peaks are shifted to the right, in agreement with [3].

For the ISU-4K mixture, an intense exothermal effect begins at 225°C. This effect is accompanied by sharp mass loss, which may be attributed to thermooxidation by ammonium nitrate. The reducing agents are organic components such as diesel fuel and coke fines.

The thermogram of the ISU-5R mixture more closely resembles that of ammonium nitrate (Fig. 3), since fewer organic additives are used in the ISU-5R than in ISU-4K mixture. In contrast to pure ammonium nitrate, however, the initial mass loss in ISU-5R mixture is accompanied by a small exothermal effect at 237°C.

For both the ISU-4K and ISU-5R mixtures, the temperature at which mass loss begins (225°C) is higher than for pure ammonium nitrate (200°C), and the eventual mass loss is more rapid. That indicates increased thermal stability.

On the basis of thermograms obtained at different heating rates, we determine the kinetic parameters of thermal decomposition in nonisothermal conditions for the ISU-4K and ISU-5R mixtures, by the Kissinger method [4]; this method was used successfully in [5, 6].

In this approach, the maximum temperature $T_{\max}$ (K) in the exothermal peak calculated from the curve for differential scanning calorimetry is related to the heating rate φ (K/s) as follows

$$\ln(\varphi/T_{\max}^2) = \ln(AR/E_a) - E_a/RT_{\max},$$

Table 2. Interpretation of Figs. 1 and 2

Effect	ISU-4K				ISU-5R				Ammonium nitrate
	heating rate, °C/min								
	2.5	5	10	20	2.5	5	10	20	10
	temperature of peak effect, °C								
Endothermal	45	50	50	57	45	50	–	55	55
Endothermal	91	95	95	96	92	94	95	99	93
Endothermal	127	132	129	133	126	130	133	136	129
Endothermal	164	167	166	167	165	166	166	169	164
Exothermal	220	236	245	252	232	237	249	261	298

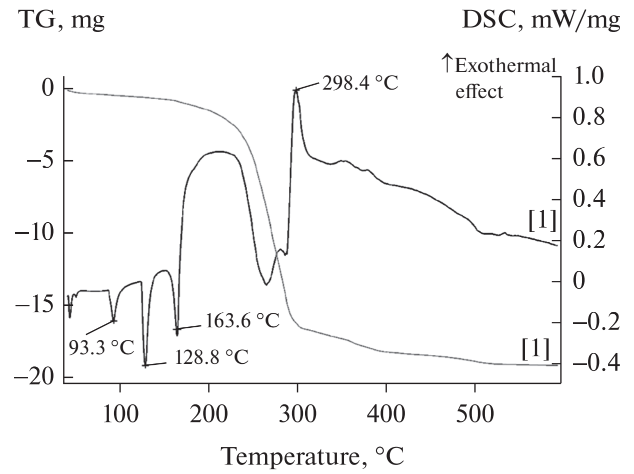

Fig. 3. Thermogram of ammonium nitrate (heating rate 10°C/min).

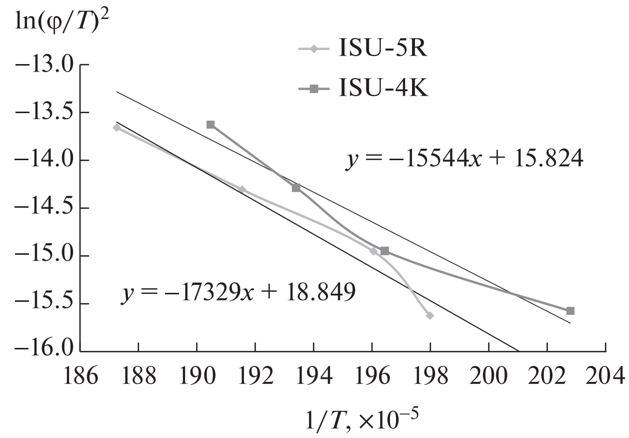

Fig. 4. Dependence of $\ln(\varphi/T_{max}^2)$ on $1/\varphi$ for the ISU-4K and ISU-5R mixtures.

where A is a constant, s^{-1}; E_a is the activation energy, J/mole; and R is the universal gas constant, J/mole K.

Table 3 presents values of T_{max} and φ for the ISU-4K and ISU-5R mixtures, as well as parameters used in plotting $\ln(\varphi/T_{max}^2)$ against $1/T_{max}$ (Fig. 4).

The slope of the straight line in Fig. 4, which is equal to E_a/R, is the coefficient in the corresponding straight-line equation (17329 for ISU-5R mixture and 15544 for ISU-4K mixture). The free term in the equation, equal to $\ln(AR/E_a)$, is 18.849 for ISU-5R mixture and 15.824 for ISU-4K mixture. Hence, for ISU-5R mixture, E_a = 144.1 kJ/mole (34.4 kcal/mole), while $\log A$ = 12.4. For ISU-4K mixture, E_a = 129.2 kJ/mole (30.9 kcal/mole), while $\log A$ = 11.1.

The flash point with different time delays is determined on the OTP certification apparatus for determining the temperature characteristics of fire safety. Samples (mass 0.5 g) are placed in a container and lowered into a working chamber heated to the required temperature within the OTP apparatus. The behavior of the samples is assessed visually by means of a mirror, and the time to ignition is determined by means of a chronometer.

The tests indicate that the flash point with 1-min delay is 349°C for ISU-4K mixture and 396°C for ISU-5R mixture.

In verification of complete combustion of the samples, the crucibles are clean at the end of combustion. In all cases, immediately before ignition, we note the copious emission of white vapor for several seconds (up to 5 s). With increase in temperature, the interval of smoke release is shorter. Above 349°C for ISU-4K mixture and 396°C for ISU-5R mixture, the samples ignite with practically no smoke release. In the combustion of ISU-4K mixture, the spark extends considerably in a vertical current of hot gases.

Table 3. Data for calculating the kinetic parameters of thermal decomposition of the ISU-4K and ISU-5R mixtures

φ, K/min	φ, K/s	t_{max}, °C	T_{max}, K	$1/T_{max}$	$\ln(\varphi/T_{max}^2)$	k, s^{-1}	$\ln k$
ISU-5R							
2.5	0.0416	232	505	0.00198	−15.627	0.00283	−5.867
5	0.0833	237	510	0.00196	−14.953	0.00555	−5.193
10	0.167	249	522	0.00191	−14.307	0.01059	−4.546
20	0.333	261	534	0.00187	−13.659	0.02025	−3.899
ISU-4K							
2.5	0.0416	220	493	0.00202	−15.579	0.00266	−5.927
5	0.0833	236	509	0.00196	−14.949	0.00500	−5.298
10	0.167	244	517	0.00193	−14.287	0.00969	−4.636
20	0.333	252	525	0.00190	−13.625	0.01879	−3.973

Table 4. Flash point of various explosives

No.	Explosive	Flash point, °C
1	ISU-4K	193
2	ISU-5R	306
3	TNT	295–300
4	Hexogen	215–230
5	TEN	205–215
6	Ammonites	280–320
7	Protective ammonites	250–350
8	Pyroxylin	195
9	Nitroglycerin	200–205

For the ISU-4K and ISU-5R mixtures, the flash point is determined at fixed temperature; in the other cases, it is determine at a heating rate of 20°C.

We also determine the minimum value of the flash point for the ISU-4K and ISU-5R mixtures. The tests are conducted by the method in State Standard GOST 12.1.044–89, analogously to the determination of the self-ignition temperature. For safety reasons, the mixture mass chosen is 0.5 g, as in determining the flash point with different time delays. For ISU-4K mixture, the flash point is 193°C; for ISU-5R mixture, it is 306°C. That is considerably less than the self-ignition temperature for pure ammonium nitrate (350°C) [7].

Thus, we may say that adding diesel fuel, coke fines, and rubber crumb to ammonium nitrate increases the thermal sensitivity of the mixtures. Note, however, that these temperatures are comparable with the flash points of commercial explosives (Table 4) [8]. Accordingly, we may regard safe use of such mixtures as feasible. In comparing the flash points in Table 4, we must bear in mind that the results determined in the present work correspond to constant temperature, whereas the flash points for the commercial explosives were determined at a heating rate of 20°C/min in [8].

In studying the mechanical sensitivity, tests are conducted with impact and with friction in rapid shear. Two types of tests are conducted, in accordance with State Standard GOST 4545–88 [9]: determination of the lower limit of sensitivity to impact in instrument 2; and determination of the explosion frequency in instrument 1. First, for the ISU-4K and ISU-5R mixtures, it is established that dropping a load (mass 10 kg, height 25 cm) in instrument 2 with a pressed charge of 50 mg does not provoke an explosion in a series of 25 tests. Therefore, to determine the lower limit of sensitivity for pressed (at 290 MPa) 100-mg samples, we drop the load from 50 cm. In all, three series of tests are conducted, each with 25 impacts. No explosion is seen in these tests, for either ISU-4K or ISU-5R mixture. Hence, the lower limit of sensitivity to impact is more than 50 cm for the two mixtures. Their level of impact sensitivity is compared with results for pure ammonium nitrate, TNT, Ammonite 6-ZhV, Alyumotol, and other explosives [10].

In instrument 1, a 10-kg load is dropped from 25 cm onto pressed 50-mg samples. Three series of tests are conducted, each with 25 impacts. For ISU-4K mixture, explosions are observed with frequencies of 36, 36, and 24%; the mean is 32%. For ISU-5R mixture, no explosions are observed. Thus, the sensitivity of ISU-4K mixture is comparable with that of Pobedit VP-4, Ammonal VA-4, Ammonite 6-ZhV, and other industrial explosives. For ISU-5R mixture, the sensitivity is comparable with that of ammonium nitrate and other explosives with practically no sensitivity.

Tests with friction in rapid shear are conducted in accordance with State Standard GOST R 50835–95 [11]. Three series of tests are conducted with 20-mg charges; the maximum load on a K-44-3 hammer is 1 GPa; and the deviation of the hammer pendulum is 110 deg. No explosion is observed in any case.

Continuing the research on mechanical sensitivity, we conduct tensometric tests, in which the explosive flash emitted is recorded by means of high-speed photodiodes, using the critical-pressure method [12]. Two series of hammer tests are conducted, recording the impact pressure profile of a 10-kg load dropped from 50 cm onto pressed charges of ISU-4K or ISU-5R mixture in instrument 2. The thickness of the charges varies from 0.05 to 1 mm. (Their mass varies from 10 to 150 mg.) The charges do not explode, but the destructive pressure is reliably recorded. As a result, the compressive strength of the charges in impact is determined: 64 MPa for ISU-4K mixture and 69 MPa for ISU-5R mixture.

Thus, tensometric tests with load impact on the explosive charges permit the determination of some rheological characteristics of ISU-4K and ISU-5R explosive mixtures under impact and confirm the finding in standard tests: no explosions are seen in instrument 2.

Comprehensive research on the mechanical and thermal sensitivity of ISU-4K and ISU-5R explosive mixtures shows that these mixtures may be successfully used in open-pit mining: their mechanical and thermal sensitivity is low.

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Translated by Bernard Gilbert

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