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Examing the selection of a fuel component for low energy mixtures
Badania w zakresie doboru materiału palnego składnika do mieszanin niskoenergetycznych

Roman Zakusylo*), Anzhela Romanchenko

Shostka Institute of Sumy State University, 1 Gagarina Street, Shostka, Ukraine
**E-mail:* r.zakusylo@ishostka.sumdu.edu.ua

Abstract: *The efficiency of an explosive mixture based on potassium chlorate(VII) (PP) with decomposition catalyst and selected combustible component was determined. The results of researches of the thermodynamic characteristics of explosive mixtures with combustible components (diesel fuel and nitromethane) are presented. Thermodynamic calculations of mixed explosives were performed using the Avakyan method. Energy and explosive characteristics such as heat of explosion, temperature of explosion, volume of gases at explosion, oxygen balance, detonation speed and explosiveness, are determined. According to qualitative and quantitative analysis of gas generation, it is established that toxic gases such as* NO_2*, CO and* Cl_2 *are present in quantities up to 0.13 mol/kg, meaning that the explosives based on PP are safe for the environment and workers in quarries.*

Streszczenie: *Określono wydajność mieszaniny wybuchowej na bazie nadchloranu potasu z katalizatorem rozkładu i wybranym składnikiem palnym. Przedstawiono wyniki badań charakterystyk termodynamicznych mieszanin wybuchowych ze składnikami palnymi (olej napędowy i nitrometan). Obliczenia termodynamiczne mieszanych materiałów wybuchowych przeprowadzono metodą Avakyan. Wyznaczane są charakterystyki energetyczne i wybuchowe, takie jak: ciepło wybuchu, temperatura wybuchu, objętość gazów podczas wybuchu, bilans tlenowy, prędkość detonacji, wysoka wybuchowość. Na podstawie jakościowej i ilościowej analizy powstawania gazów podczas wybuchu ustalono, że gazy toksyczne takie jak* NO_2*, CO i* Cl_2 *występują w ilości do 0,13 mol/kg, w wyniku czego kompozycje wybuchowe oparte na nadchloran potasu są bezpieczne dla środowiska i pracowników kopalni odkrywkowych.*

Keywords: *potassium chlorate(VII), diesel fuel, nitromethane, heat of explosion, volume of explosion gases, detonation velocity*
Słowa kluczowe: *chloran(VII) potasu, olej napędowy, nitrometan, ciepło wybuchu, objętość gazowych produktów wybuchu, prędkość detonacji*

Abreviations:

DF	Diesel fuel
NM	Nitromethane, CH_3NO_2
PP	Potassium chlorate(VII), $KClO_4$

1. Introduction

Decorative stone is widely used in various sectors of the economy such as architecture, construction, artistic stonemasonry. At the moment, mainly explosive, chemical and physico-chemical extraction methods of block stone are used. Despite the large losses of valuable useful raw materials during mining, explosive technologies and means of stone cleaving due to their high productivity continue to be used and improved around the world [1].

Potassium chlorate(VII) (PP) was selected as an oxidant in the development of pyrotechnic compositions for the implementation of industrial blasting works on the cleaving of block stone. PP has a number of advantages in use, but it decomposes with a very small amount of heat and therefore explosive decomposition in compositions with PP occurs and spreads with great difficulty. The question of decomposition of mixtures based on PP is quite extensive and deep. It has been proved theoretically that oxides of some metals enhance the catalytic effect of PP decomposition [2, 3]. In order to reduce the decomposition temperature of explosive mixtures on the base of PP in accordance with kinetics studies of its thermal decomposition, a catalytic entity − manganese oxide(IV) (MnO_2) was selected [4].

In practice, the use of thermodynamic calculations allows new types of explosives to be created by pre-assessing the performance of the mixtures. Thus, to achieve the conditions of a „soft" explosion, and as a consequence of ensuring economical reflection of blocks without damage, mixed explosives must have a low detonation velocity (not more than 2000 m/s), low heat of explosion and a minimum amount of gaseous products. This will ensure high-quality separation of the block from the array without cracks and the absence of fragmentation [6].

The mixture of PP with the decomposition catalyst without combustible components when initiated by the electric detonator ED-8, does not go to a stable detonation mode. Due to this, there was a need to use a fuel component. This also leads to organoleptic property improvements and caking reduction, which generally improves exploitative characteristics.

In the paper, the most important factors [5] in the implementation of mixed explosives include indicators of theoretical energy are the heat of explosion, the velocity of detonation, the volume of gases in the explosion, high explosiveness, detonation pressure, have been presented. Based on literature analysis, diesel fuel (DF) and nitromethane (NM) were selected as combustible components for further research.

2. Experimental

2.1. Thermodynamic calculations of low-energy substances using the Avakyan method

Thermodynamic calculations of developed industrial explosive substances by Avakyan's method, which allows the study of the energy and explosive characteristics of explosives, were determined [7]. The amount of explosive transformation gases was determined by Avakyan's method, which is implemented in the multi-purpose application program „Astra" – „Modeling of chemical and phase equilibria at different temperatures". At the first stage of research of the developed compositions, thermodynamic calculations such as: heat of explosion, temperature of explosion, volume of gases at explosion, oxygen balance, detonation velocity, explosiveness, etc. are carried out [7].

2.2. Materials

Preliminary preparation of explosive mixtures for the experimental research to determine the physico-chemical and explosive characteristics, consisted of preliminary preparation of components (drying, sieving) and their mixing. PP has low hygroscopicity, but was dried at 358 K for 3 h. The PP was then sieved to exclude any grains larger than 100 µm. MnO_2 was dried and passed through a sieve with a hole diameter of 50 µm. The degree of purity and the corresponding standards for possible contaminants for PP and other components are given in the Table 1.

Table 1. The degree of purity and the corresponding standards for possible contaminants

No.	Component	Regulations	Purity grade	Mass fraction of the main component, not less than [wt.%]
1	PP	TC 6-09-3801-76, TC 2147-471-05121441-2008	pure for analysis	99.5
2	MnO_2	STST 4470-79	pure for analysis	90
3	DF	STST305-82	S-0.2-40, the highest grade	–
4	NM	TC 6-09-11-876-77	pure	–

Diesel fuel (DF), liquid petroleum fuel, is a mixture of hydrocarbons. It is obtained from kerosene-gas-oil fractions by the direct distillation of oil. Diesel fuel refers to low-toxic substances. The maximum permissible concentration of fuel vapour in the air of the working area is 300 mg/m^3. The explosive concentration of its vapor and mixture with air is 2-3 vol.%. The auto-ignition temperature of the fuel is 300-330 °C [8]. The component composition of mixed explosives based on PP is shown in Table 2. Based on the results of thermodynamic calculations presented in Table 3, a rational composition with characteristics which meet the requirements for low-speed explosives, will be selected.

Table 2. Component composition of mixed explosives based on PP

No.	Component	Numbers and composition of samples of mixed explosives [%]							
		1	2	3	4	5	6	7	8
1	PP	90.5	92.5	93.5	94.5	95.5	96.5	97.5	99.5
2	MnO_2	0.5							
3	DF	9	7	6	5	4	3	2	–

Table 3. Thermodynamic characteristics of explosive mixtures based on PP

Parameter	Sample numbers and their characteristics							
	1	2	3	4	5	6	7	8
Oxygen balance [%]	20.81	26.3	26.77	31.57	34.90	37.77	40.64	45.71
Heat of explosion [kJ/kg]	2695	2486	2348	2205	2110	2065	1897	1235
Explosion temperature [K]	3000	2810	2536	2207	2107	2003	1395	1957
Volume of gases [l/kg]	512	426	377	348	317	302	298	346
Detonation velocity [m/s]	3100	2530	2410	2091	1980	1710	1689	1240
High explosiveness [ml]	156	117	99	89	93	85	67	55

Nitromethane (NM), CH_3NO_2, a simple nitro compound of the aliphatic series, has a low sensitivity to impact (when tested on copra − 0-8% of the operation for a weight of 10 kg at a drop-height of 25 cm) and friction, and is sensitive to fire.

Nitromethane in pure form has a fairly large critical diameter and low sensitivity to detonation. N is not a flammable substance, with careful inflammation burns. It becomes explosive when heated above its boiling point of 101.2 °C (374.35 K). It is not sensitive to detonator cap No. 8. Regarding its harmful effects on the human body, it belongs to the 4th class of danger, the allowable concentration of vapor in the air (MPC) being – 30 mg/m^3 [9].

The explosive decomposition of NM proceeds according to the equation [10]:

$$CH_3NO_2 \rightarrow 0.2CO_2 + 0.8CO + 0.7H_2O + 0.5N_2 + 10531 \text{ kJ/kg} \quad (1)$$

The maximum decomposition temperature reaches the value of 2450 K.

3. Results and discussion

3.1. Optimization of the chemical composition

To perform thermodynamic calculations, hypothetical formulations based on PP and decomposition catalyst – MnO_2 were selected. DF has also been used as an additional fuel. Based on an analysis of the thermodynamic calculations, a logical recipe for the pyrotechnic composition was selected, meeting the requirements for explosives for the extraction of block stone. The mixture includes the following components:
- PP: 94.5%,
- MnO_2: 0.5%,
- DF: 5.0%.

In the second stage of research, NM was used in the composition of industrial explosives. To perform thermodynamic calculations of mixed explosives composition for quarying of block stone, hypothetical formulations based on PP and decomposition catalyst − MnO_2, were selected. As an additional fuel, as well as to improve organoleptic properties and reduce caking, aliphatic nitro compound NM was used.
The component composition of mixed explosives based on PP is shown in Table 4. Based on the results of thermodynamic calculations presented in Table 5, a logical composition was selected. It meets the requirements for explosives for the extraction of block stone.

Table 4. Component composition of mixed explosives based on PP

Component	Numbers and composition of samples of mixed explosives [%]									
	1	2	3	4	5	6	7	8	9	10
PP	96.5	94.5	92.5	90.5	89.5	86.5	84.5	82.5	79.5	99.5
MnO_2	0.5									
NM	3	5	7	9	10	13	15	17	20	–

Table 5. Thermodynamic characteristics of explosive mixtures based on PP

Parameter	Sample numbers and their characteristics									
	1	2	3	4	5	6	7	8	9	10
Oxygen balance [%]	42.18	39.66	37.14	35.07	33.35	30.37	27.04	24.52	20.73	45.81
Heat of explosion [kJ/kg]	486.4	508.2	672.3	756.7	858.1	1069.7	1272.5	1381.5	1496.4	1235
Explosion temperature [K]	1068	1253	1387	1435	1523	1693	1853	1985	2065	1957
Volume of gases [l/kg]	325	346	358	368	374	387	399	417	453	346
Detonation velocity [m/s]	870	990	1214	1326	1550	1620	1700	1786	1835	1240
High explosiveness [ml]	83	87	89	90	93	97	102	108	116	55

According to the analysis of thermodynamic characteristics, it follows that the ratio of potassium perchlorate to nitromethane at 90 to 10 meets the requirements of the composition for the reflection of block stone. This ratio of components provides low values of temperature and heat of explosion. The volume of gaseous products of explosion is at the level of 370 l/kg and a detonation velocity of up to 1550 m/s provides a „saving" reflection of the block stone.
The mixture includes the following components:
− PP: 89.5%,
− MnO_2, :0.5%,
– NM: 10.0%.

The main safety characteristic of these compositions is that PP, MnO_2, DF and NM are not explosives individually and only form an explosive when they are combined.

3.2. Quantitative and qualitative determination of gaseous products of explosion

The next step in the study is to determine the explosion products of mixtures based on PP, decomposition catalyst and combustible component, which can use DF or NM. An explosion is an irreversible reaction which converts an initial substance or mixture of substances into gaseous products of an explosion. Based on this, it is necessary to take into account the fact that a large volume of gas is formed during blasting. The explosion is based on the oxidation of combustible substances by oxygen, and therefore the composition of mixed explosives must be made in such a way that the explosion produces products which pose minimal danger to miners.

In order to determine the amount and composition of gases generated during the explosion of low-energy mixtures based on PP, calculations on the multi-purpose program „Astra" – „Modeling of chemical and phase equilibria at different temperatures", were performed. The program is based on a universal thermodynamic method for determining the equilibrium characteristics of heterogeneous systems. It is based on the fundamental principle of maximum entropy and allows you to calculate the number and composition of gaseous products of combustion and explosion.

Calculations for the formation of gases were first performed for mixtures of PP with MnO_2 as a decomposition catalyst. The results of the calculations show that in the explosion of P3 with decomposition catalysts, the final products have a significant amount of oxygen (14.073 mol/kg), because the mixture has a positive oxygen balance and KCl (6.787 mol/kg). Other decomposition products are present in small quantities (O – 0.252 mol/kg, K – 0.1570 mol/kg, Cl – 0.0906 mol/kg, KO – 0.0306 mol/kg, MnCl – 0.0565 mol/kg). Thus, the decomposition of PP in an explosion can be represented by the reaction:

$$2KClO_4 \rightarrow 2KCl + 4O_2 + Q \qquad (2)$$

Thus, based on the above data, it can be concluded that the mixture of PP with decomposition catalysts, in terms of the formation of gaseous products of the explosion is safe for the environment and workers.

The next step is the qualitative and quantitative determination of the explosion products of mixtures of PP, catalyst together with fuel, which can be used with diesel fuel or NM. The gas composition of PP was also determined for comparison. In order to assess the composition of gaseous products of the explosion of industrial explosives using different types of combustible component, the amount and composition of gases emitted during the explosive transformation of mixed explosives for low-energy charges, appropriate calculations were carried out (Table 6). These are based on universal thermodynamic methods for determining equilibrium characteristics of heterogeneous systems.

Table 6. The content of gaseous products of the explosion of the compositions of PP with diesel fuel and NM

No.	Gaseous product	The amount of gases [mol/kg]		
		100% PP	94.5% PP, 5% DF, 0.5% MnO_2	89.5% PP, 10% NM, 0.5% MnO_2
1	H_2O	–	4.053	2.03
2	O_2	14.296	5.922	11.51
3	KCl	7.0548	6.27	6.14
4	Cl_2	0.0006	0.0004	0.13
5	CO	–	0.265	0.081
6	NO_2	–	–	0.002
7	N_2	–	–	0.73
8	HCl	–	0.266	0.17
9	CO_2	–	2.451	1.55
10	H_2	–	0.437	–
Total:		21.3514	19.6644	22.343

From the results of the calculations it is clear that during the explosion of PP with DF and decomposition catalysts, the final products contain a significant amount of oxygen (namely 5.922 and 11.51 mol/kg, respectively, because the mixture has a positive oxygen balance) and KCl. The estimated amount of oxygen in the case of the study of the PP sample is 2 times higher than that of the test sample with the introduction of the fuel component. This is due to a decrease in the oxygen balance of the system due to the use of the fuel component. In this case, carbon is largely oxidized to CO_2, hydrogen to H_2O. Toxic gases such as CO and Cl_2, which have the ability to adversely affect the human body, including death, are present in small amounts (up to 0.265 mol/kg).
The main products of the explosion of PP-NM are KCl and oxygen (because the oxygen balance is 33.35%). Carbon is almost completely oxidized to CO_2, hydrogen to H_2O. Toxic gases such as NO_2, CO and Cl_2 are present in small quantities – up to 0.13 mol/kg.
Thus, the above data, in accordance with the maximum permissible concentrations of harmful gases in the environment, confirm that mixtures of potassium perchlorate with decomposition catalysts, as well as fuel in the form of diesel fuel or nitromethane, are safe for the environment in terms of toxic gaseous products, and also for workers in quarries.
In addition, to ensure long-term storage, safety during industrial blasting works with industrial explosives, achieving the conditions of „soft" reflection of block stone and the reliability of operation from the standard means of initiation, the experimental and calculated physico-chemical and energy characteristics of charges based on PP were determined. The results are given in Table 7.

Table 7. Physico-chemical and thermodynamic characteristics of the composition based on PP

No.	Parameter	Values for mixtures with	
		DF	NM
1	Oxygen balance [%]	+25.67	+37.7
2	Heat of explosion [kJ/kg]	2165.8	858.1
3	Explosion temperature [K]	2003.65	1523
4	Volume of gaseous products of explosion [l/kg]	334.4	374
5	The density of the composition [g/cm^3]	0.99-1.02	1.05-1.10
6	Sensitivity to impact according to GOST 4545, frequency of explosions in the device 1 [%]	36	41
7	Sensitivity to friction in the device K-44-3 [kg/cm^2]	3650	3740
8	High explosiveness [ml]	85	95
9	TNT equivalent	0.51	0.55
10	Critical detonation diameter [mm]	5-19	10-12
11	Detonation velocity [m/s]	1800-2100	1000-1555

From the analysis of the data in Table 7, we conclude that the characteristics of the compositions meet the requirements for low-energy charges for the reflection of block stone. In addition, it is experimentally confirmed that the charges based on the developed mixtures initiate reliably from the standard means of initiation such as electric detonators ED-8 and detonating cord DCE-12. Given this and the low sensitivity to mechanical stimuli, the compositions can be used as a means of reflecting block stone.

4. Conclusions

- ♦ Thermodynamic calculations were performed in accordance with Avakyan's method for the purpose of preliminary assessment of the efficiency of the compositions of mixed low-energy explosives based on PP. Based on the calculations of oxygen balance, energy and explosive characteristics, the proposed compositions of heterogeneous condensed systems based on PP, corresponding to the ratio of components: 94.5% PP, 5% DF and 0.5% MnO_2 in the first case; 89.5% PP, 10% NM and 0.5% MnO_2 –

in the second. These explosives are rational to use for "saving" extraction of block stone in granite and labradorite quarries.

- ♦ Based on the qualitative and quantitative analysis of gas formation during the explosion of the developed low-energy systems, it is determined that toxic gases such as NO_2, CO and Cl_2 are present in amounts up to 0.13 mol/kg.
- ♦ As a result, PP-based explosives are safe for the environment as well as for workers in quarries. When comparing the two investigated combustible components in terms of the formation of gaseous products of the explosion, physico-chemical and detonation parameters, diesel fuel is a more rational combustible component. In addition, its use in low-energy mixtures is more cost-effective than NM.

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