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Explosive composition on the basis of potassium perchlorate and nitromethane

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Abstract

The presented results of researches are on development of explosive composition of pyrotechnic type on the basis of non-explosive components such as potassium perchlorate and nitromethane. On the basis of thermodynamics calculations the correlation of potassium perchlorate and nitromethane was determined as 90:10 that provides the quality descriptions of explosive composition for soft breaking of sectional stone: the detonation speed of 1300 m/s, detonation critical diameter of not more than 12 mm, the explosion gases volume to 370 l/kg. Physically chemical and explosive descriptions were experimentally determined. It is suggested to manufacture the explosive composition directly on the

places of explosive works realization. This allows increasing the safety in the manufacture and use of explosive composition, as it does not require the transportation of explosive components on the roads of Ukraine.
Key words: EXPLOSIVE COMPOSITION, POTASSIUM PERCHLORATE, NITROMETHANE, THERMODYNAMIC CALCULATIONS, EXPLOSIVE CHARACTERISTICS

Ukraine has considerable reserves of decorative stone (labradorite, andesites, gabbro, etc.) with unique decorative properties [1]. The decorative stone is widely used in the manufacture of monuments, art products, construction and facing works. Unlike other methods of extracting minerals (iron ore, coal, construction rocks) the obtaining of decorative stone using the blasting method must ensure the preservation of the value of the decorative stone (no cracks) and monolithic array of minerals.

For breaking of the decorative stone the explosives with low detonation speed (no more than 2000 m/sec) and the minimum amount of gaseous detonation products are required, that will provide the high quality of the block breaking from the array without cracks and lack of crumbs of the valuable stone. Currently in Ukraine for breaking of the block stone black powder is used, which although provide the satisfactory production of decorative stone, however, has high hygroscopicity and is dangerous to use due to the high fire risk and the mechanical stress sensitivity such as impact and friction and therefore it requires the replacement. Thus, the development of the explosive composition, which will provide the breaking of natural stone blocks from the array by soft and effective way, while maintaining the technological and decorative properties of the raw material at high level, is actual question.

The authors propose an explosive composition of pyrotechnic type based on the potassium perchlorate as oxidizer and diesel fuel as the fuel [2]. The developed composition has the detonation speed of 2000 m/s, the critical detonation diameter of 18-20 mm and the volume of gaseous explosion products of 320 l/kg. For better breaking of the decorative stone the explosive composition with the value of the critical diameter of 12-13 mm and a detonation velocity of 1500 m/s are required. In addition such explosive composition should provide the reliable triggering from the standard means of initiation such as the detonating cord and capsule-detonator ED-8.

For this purpose it is planned to upgrade the known explosive composition in terms of research to use nitromethane as a fuel. Nitromethane (NM), CH_3NO_2 [3], is the easier nitro compounds from the aliphatic series, colorless liquid with an odor of bitter almonds, the boiling temperature is 101.2 ° C, melting temperature is minus 29 ° C, the vapour flash point in an open crucible is 45 °C, the density is 1.138 g/cm^3, it is soluble in water (10.5 %), creates an azeotropic mixture with water (76.4 % of nitromethane and 23.6 % of water). It is mixed with the common organic solvents (except paraffins), it is a good solvent for many organic and inorganic substances. It has some sensitivity to shock (when tested at the copper - 0-8% positives for weight of 10 kg at the drop height of 25 cm) and it is friction sensitive to fire.

Nitromethane in its pure form has a sufficiently large critical diameter and low sensitivity to detonation. Nitromethane is not flammable, while careful the ignition it is on fire. It becomes explosive when is heated above the boiling point. It isn't sensitive to the primer-detonator No.8. According to the hazard effects on the human body it refers to the 4th class of danger, the permissible concentrations of vapours in air MAC is 30 mg/m^3. In industry the nitromethane usually is received by the destructive nitration of propane. Nitromethane is used in industry as an additive to motor fuels for the purpose of increasing their energy characteristics (octane number), or as fuel in aircraft modeling sport.

The explosive schedule of nitromethane proceeds according to the equation:

$$CH_3NO_2 = 0{,}2CO_2 + 0{,}8CO + 0{,}7H_2O + 0{,}5N_2 + 10531 \text{ kJ/kg} \quad (1)$$

The maximum decomposition temperature reaches 2177 °C.

The studies of thermal decomposition of nitromethane and its mixture with potassium perchlorate using the differential thermogravimetrical analysis were conducted on derivatograph Q-1500 D of F. Paulic, J. Paulic, L. Erdey Production Company.

It was established that nitromethane and potassium perchlorate are chemically compatible, as while the analysis thermal decomposition curves of the mixture (Figure 2) and the individual components (Figure 1), the subsidiary peaks that signal the components chemical interaction were not founded. Thus, nitromethane as combustible component facilitates

the PP thermal decomposition, resulting in lowering of the PP - NM mixture decomposition temperature up to 300 ^{0}C, in comparison with PP.

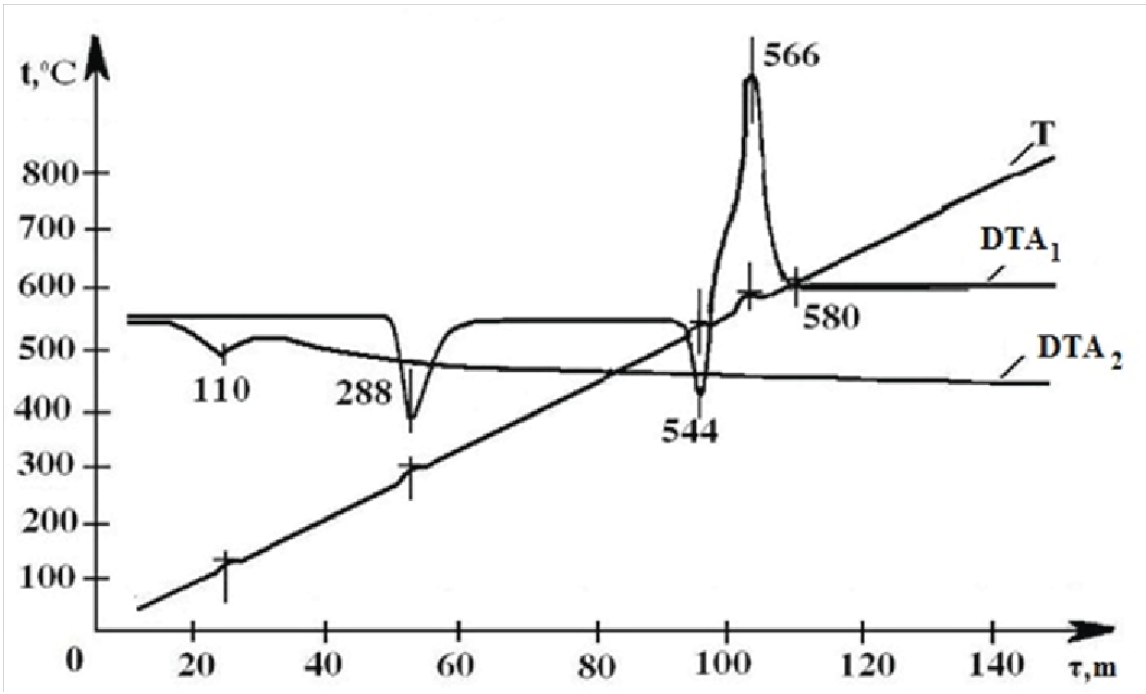

Figure 1. The thermograms of decomposition of: DTA_1 – PP, DTA_2 - NM

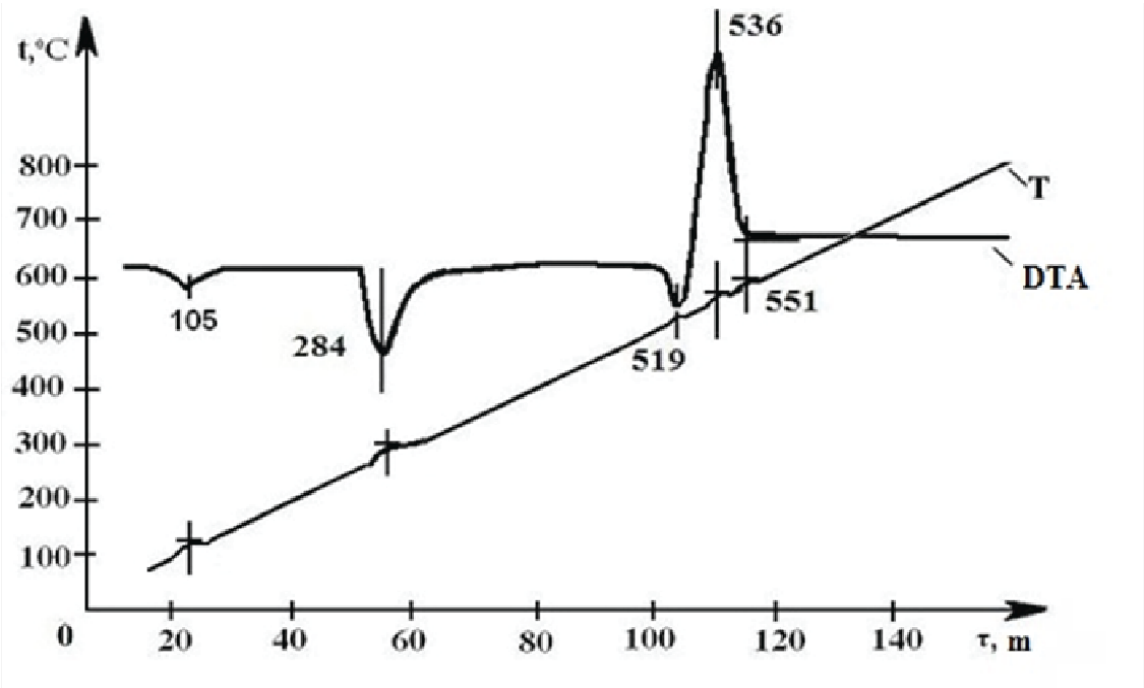

Figure 2. The thermogram of decomposition of PP + NM

To select the optimal ratio of components that will provide the thermodynamic and explosive characteristics according to the requirements of the explosive composition for breaking of block stone, thermodynamic calculations PP-NM system – by Avakyan method [4] were carried out.

Table 1. The composition and calculated characteristics of explosive mixtures based on $KClO_4$ and nitromethane

Name of the component	Number and composition of the samples		
	1	2	3
PP with 0.5% of Fe_2O_3	95	90	85

Nitromethane	5	10	15
Characteristics	Calculative values		
The oxygen balance, %	+41.9	+37.7	+33.4
The explosion heat, kJ/kg	508.2	858.1	1272.5
The explosion temperature, K	1253	1523	1853
The volume of gases, l/kg	346	374	399
Detonation speed, m/s	990	1550	1700

It follows according to calculations that the ratio of potassium perchlorate to nitromethane as 90 to 10 corresponds best to requirements for compounds breaking of block stone. This ratio of components provides the low values of temperature and explosion heat. The volume of gaseous explosion products is about 370 liters/kg and the detonation speed is less than 1.550 m/s, this fact will provide "soft" breaking of the block stone.

Determining of the composition and gaseous products quantity, which are released during the explosion, were calculated using the program "Astra" - "Modeling the chemical phase balance at different temperatures". The calculation results are shown in the table 2.

Table 2. The content of gaseous explosion products of PP and NM compositions

The composition of gases	Number of gases, mol/kg		
	PP +5% of NM	PP +10% of NM	PP +15% of NM
H_2O	0.93	2.03	3.16
O_2	12.83	11.51	10.14
KCl	6.49	6.14	5.68
Cl_2	0.11	0.13	0.11
CO	0.038	0.081	0.13
NO_2	0.0017	0.002	0.0023
N_2	0.34	0.73	1.12
HCl	0.12	0.17	0.21
CO_2	0.78	1.55	2.32

From the calculations results it follows that the main products of the explosion of PP and NM compositions are KCl and oxygen (as oxygen balance of compositions is high enough). Carbon is almost completely oxidized to CO_2, H_2O into hydrogen. The toxic gases such as NO_2, CO and Cl_2 are present in small quantities.

The prototypes of explosive composition with different components content were manufactured for experimental verification of the developed structure. Potassium perchlorate was dried in the heat cabinet at 70 ± 5 °C to the moisture content of less than 0.2%. After drying it was ground in the ball mill and sifted through the sieve with the hole diameter of 400 microns. Metal oxide, in this case iron (III) oxide Fe_2O_3, was grinded through the sieve with the diameter of holes 100 microns to remove the lumps. The explosive composition components were mixed in laboratory mixer with Z-shaped blades. First potassium perchlorate was charged, and then decomposition catalyst was added and stirred for 20 minutes. Nitromethane does not require the supplementary training.

PP and nitromethane are not explosive materials separately. The mixture becomes explosive only after mixing of the components. The prepared potassium perchlorate with the decomposition catalysts and nitromethane in separate packages were transported as not explosive components on the research site for explosion characteristics determination. To obtain explosive mixtures the mixing of the components was performed in plastic container (bucket): first bombarded the potassium perchlorate with decomposition catalyst, and then while stirring with the wooden spatula nitromethane was added. Mixing of PP and

NM and at the quarry will be conducted in the mixer with z-shaped blades. After mixing of the explosive mixture components the explosive properties were determined: critical diameter of detonation, detonation speed and completeness of detonation [5].

Critical diameter of detonation of the explosive composition was assessed using method of cone: the cone of paper for patterning with the cone angle of 5^0 was filled with an explosive compound and blew up by the regular means of initiation. The values of the detonation critical diameter of the explosive composition have been set according to unexploded portion of the cone. The detonation speed was determined by the Dotrice method. The detonation completeness was determined on cylinders made of paper for patterning with the diameter of 20% larger than the detonation critical diameter. The completeness of detonation was assessed by the absence of explosive composition residues after the explosion and availability of dents in the plate-witness. Initiation was carried out from electrodenerator ED-8. In all cases, explosive compositions detonated reliably. Explosive characteristics of the compositions are shown in the table. 3.

Table 3. Experimental explosive characteristics of the composition PP – NM

Name of the components	Number and composition of the samples		
	1	2	3
PP with 0.5% of MnO_2	95	90	85
Nitromethane	5	10	15
	Experimental characteristics		
Detonation critical diameter, mm	27	12	3-5
Speed of detonation, m/s	~1000	1300	1550
Completeness of detonation	full	full	full

On the basis of thermodynamic calculations and experimental studies the formulation of the explosive composition was selected with the ratio of potassium perchlorate and nithromethane as 90:10, the characteristics of which are given in table 3. Such explosive composition has the detonation speed at the level of 1300 m/s at the detonation critical diameter of not more than 12 mm and the low volume of explosion gaseous products. These characteristics will provide the quality breaking of the decorative block stone, preventing the occurrence of cracks and damage.

Table 4. Physic-chemical and explosive properties of the composition PP: NM – 90:10

Characteristics	Value
Oxygen balance, %	+37.7
Explosion heat, kJ/kg	858.1
The explosion temperature, K	1525
The volume of gases, L/kg	347
Mass density, g/cm^3	1.05-1.10
TNT equivalent	0.85
Sensitivity to impact GOST 4545, the frequency of explosions in the instrument №2, %	29
Friction sensitivity in the instrument K-44-3,mPa (kg/cm^2)	360 (3600)
Detonation critical diameter, mm	12
Speed of detonation, m/s	1300

Conclusions

The low-velocity explosive composition on the basis of the potassium perchlorate as oxidizer and nitromethane as the fuel component at the ratio of 90:10 was developed. Since the mixture has the detonation speed of 1300 mm/s, explosion heat of 858 kJ/kg and the low volume of detonation gaseous products, it can be used for qualitative breaking of the decorative block stone. The main safety feature of the developed composition lies in the fact that the potassium per-

chlorate and nitromethane separately are not explosives and only when the components are mixed, the composition acquires explosive characteristics. The explosive composition of the non-explosive components is offered to produce directly in the field of blasting, i.e. at the quarry. This will prevent the transport of explosive compounds from the manufacturer by the special transport on the territory of the country, because of the danger to the public, approval of the route with the traffic police or security threat of explosive cargo and reduce the amount of protected storage facilities for explosive materials on points at the quarry.

References

1. Iskov S.S. (2004) The features of development of deposits of decorative stone, and the value of the geometrization of the basic properties for the improvement of mining blocks technology. Bulletin of Zhitomir Technological University, No 3 (30), 2004.
2. Patent 68559 U Ukraine MPK6 C 06 B 31/28. Explosive composition. Zakusylo, V.R., Efymenko, A.A., Romanchenko, A.N. No 201112120, bulletin No 6, 2012.
3. Orlova E.J. Chimija i technologija brizantnyh vzryvchatych veschestv [Chemistry and technology of high explosives]. Chemistry, 1981, 358 p.
4. Avakjan G.A. Raschet energeticheskich i vzryvchatych charakteristik VV [The calculation of the energy and explosive characteristics of explosives]. Moscow, Academy of engineering, 1964.
5. Patent 100445 U Ukraine MPK6 C 06 B 31/28. Explosive composition. Zakusylo, V.R., Romanchenko, A.N., Zakusylo, R.V. No 201501015, bulletin No 14, 2015.

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Radial-direct extrusion with a movable mandrel

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Abstract

With the aid of grade grids method the character of strained condition and features of forming hollow parts when combined radial-direct extrusion were distinguished. By the upper- bound method the mathematical models of the radial-direct extrusion on the conical mandrel were developed. The