INNOVATIVE FORMULATIONS FOR A NEW GENERATION OF LOW-SPEED EXPLOSIVE COMPOSITIONS, DESIGNED FOR BLASTING IN TENDER CONDITIONS AND FOR EXTRACTION OF ROCK-CLADDING MATERIALS

Nadezhda Stoycheva, Peter Shishkov

University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; sfxman86@yahoo.com

ABSTRACT. There are some fields in mining, or construction at industrial and urbanised territories, where application of regular commercial explosives and high explosives is not enough safe for the surrounding objects with regard to the generated fly-rocks, air-blast, toxic fumes, seismic waves and vibrations. The main reasons for these harmful impacts of explosion are the velocity and mechanism of the chemical reaction of explosive mixture's decomposition. The industry redirects its attention from the detonating explosives to the deflagrating pyrotechnic mixtures and propellant compositions. Utilisation of aged military arms is a good source of cheap materials for the explosive industry. The production of low explosive non-detonating mixtures from long term stored single base propellants (SBP), double base propellants (DBP) and ammonium nitrate prills in different configurations, as well as popular flash-powder compositions was studied. The samples of different cartridge casings, filled with non-detonating propellant mixtures, or flash-powder compositions was investigated by two methods for velocity of propagation. The blasting cartridges were made from the investigated materials and were examined via field tests. General information on dimension stones as well as brief information about the explosives involved in their extraction is presented.

Keywords: non-detonating blasting cartridges, single base propellants, double base propellants, cautious blasting, dimensional stone extraction

ИНОВАТИВНИ РЕЦЕПТУРИ ЗА НОВО ПОКОЛЕНИЕ НИСКО-СКОРОСТНИ ВЗРИВНИ СЪСТАВИ, ПРЕДНАЗНАЧЕНИ ЗА РАЗРУШАВАНЕ В УСЛОЖНЕНИ УСЛОВИЯ И ПРИ ДОБИВ НА ДЕКОРАТИВНИ КАМЪНИ

Надежда Стойчева, Петър Шишков
Минно-геоложки университет "Св. Иван Рилски", 1700 София

РЕЗЮМЕ. Съществуват области в минното дело или при строителството в индустриални и урбанизирани територии, където прилагането на обичайните промишлени експлозиви не е достатъчно безопасно за околните обекти, по отношение на разлет на късове, ударно-въздушна вълна, токсични газове, сеизмични вълни и вибрации. Основната причина за вредното въздействие на експлозията са скоростта и механизма на протичане на химичната реакция при разпадане на взривната смес. Промишлеността пренасочва вниманието си от детониращите експлозиви към дефлагриращите пиротехнически смеси и барутни състави. Утилизацията на остарели или ненужни боеприпаси е добър източник на евтини материали за взривната промишленост. Беше изследвано производството на ниско-скоростни (недетониращи) взривни смеси от продължително съхранявани едноосновни и двуосновни барути и порьозна амониева селитра в различни съотношения, както и звуково-светлинни пиротехнически състави. Проби от различни корпуси, напълнени с недетониращи барутни смеси, или пиротехнически състави бяха тествани чрез два метода за скорост на взривяване. От изследваните материали са изработени взривни патрони, с които са проведени полеви изпитания. Представена е обща информация за декоративните камъни, както и кратка информация за експлозивите, използвани за техния добив.

Ключови думи: недетониращи взривни патрони, едноосновни барути, двуосновни барути, прецизно взривяване, добив на скално-облицовъчни материали

Introduction

About explosive chemical decomposition

The velocity of detonation (VOD) is the rate at which the detonation wave moves through the explosive charge. The higher this speed, the greater the "force" or the crushing effect of the explosive. Explosives with high chemical decomposition rates are better suited to working on hard rocks, and those with a slower detonation to work in a soft and cracked rock. In general, "low-speed" explosives tend to release gaseous products for a relatively longer period of time, and therefore, its action is more "heave". The detonation rates of different industrial explosives are between 2500-7500 m/sec. The detonating pressure is the pressure in the reaction zone when the explosive molecules break down. The last is an important indicator of the explosive's ability to perform a good fragmentation.

Deflagration is a subsonic reaction of the chemical decomposition of the explosives. It is typical of all types of gunpowder and solid rocket fuel. They act on the environment by the pressure generated by gaseous products during a chemical reaction and practically have almost no "shock energy". In practice, such an effect occurs when a charge of blasting gunpowder is ignited in an appropriately tamped blast hole.

Dimension stone extraction and blasting in tender conditions

Rock cladding materials is a common term for various natural stones used for construction or for decorative purposes in buildings and monuments. The determining characteristic of a dimension stone is that, unlike other mineral raw materials, which have a value mainly due to their physical properties, the physical properties of the rock are only the minimum qualification to determine its suitability for use as a rock cladding material. Some authors prefer the term "decorative stone", which emphasises the ornamental aspect of its use. In fact, the rock cladding material is defined as “a natural rock material cut, shaped, or selected for use in blocks, slabs, sills or other structural elements with specialised shapes and sizes”. Therefore, the decorative stone has a value due to its size and appearance, emphasised by a set of minimal physical properties (among them are various strength parameters, workability, polishing ability and resistance to physical and chemical influences).

The use of explosives in quarries for decorative stones is a rather delicate issue. During the extraction of rock-cladding materials, drilling and blasting operations are carried out, both for removal of poor layers of soil and rocks (stripping) and for the initial separation of large slabs from the rock body and their splitting into smaller blocks suitable for transporting and post-processing of finished products. Across the globe, popular industrial explosives are used to break up unnecessary rock and soil layers, but when approaching high-quality stone deposits, blasting technologies must be more precise and prevent costly material from being destroyed.

In such cases, the high explosives are successfully replaced by low-velocity explosives. There are other areas in the mining industry or in construction in industrial and urban areas, where the use of ordinary industrial explosives is not safe enough for surrounding sites in terms of fly-rocks, shockwave formation, toxic gases, seismic waves and vibration. The main cause of the detrimental effect of the explosion is the speed and mechanism of the chemical reaction of the explosive mixture decomposition. It is exactly the detonation that causes the fragmentation and the formation of cracks in the rock body. The surfaces of the stone blocks must not be deeply damaged by the blast wave with micro-cracks, as this will lead to financial losses due to the high value of the qualitative decorative stones. They should only be affected by the creation of single cleavage cracks in one, two or three planes, depending on the technological needs. Therefore, the use of industrial explosives and high-explosives for dimension stone extraction is not preferred by the owners of such quarries.

The industry is shifting its attention from detonating explosives to deflagrating pyrotechnic mixtures and propellant compositions, which suddenly create a large volume of compressed hot gaseous products with no shock wave and really little solid residue. The charges of these new explosives must be resistant to moisture, shock, heat, friction and electrical discharge. In the past, the usual solution was the black powder. The so called “blasting gun powder” (BGP) was applied orderly for dimensional stone extraction and in other cases - for cautious blasting in tender conditions. But its sensitivity to various influences (flame, heat, moisture, friction, shock) in combination with the lower energy of reaction, the toxic fumes and the solid products induced scientific research for more advanced and safer alternatives. Nowadays, the most important requirement of the industry to the explosive manufacturers is the safety of their products regarding storage, transportation and usage. Another important question is the price. Utilisation of aged military arms is a good source of cheap materials for the explosive industry.

Waste smokeless gunpowders

It is well known, that single based propellants (SBP) in general are pelletized or extruded porous grains in different sizes and shapes, which usually contain 93-97% pyroxylin and 3-6% additives like dibutylphtalate or dimethylacrylate or camphor (phlegmatizers), diphenylamine (stabilizer), KNO_3 or K_2SO_4 (pore-forming salt), graphite, remaining alcohol-ether solvent, etc. DBP are mixtures of nitrocellulose (NC), 2-8% additives (similar to these in SBP) and nitro-esters usually nitro-glycerine (NG). The content of NG is about 10-38%. The boiling point of NG is 50^0C. Double base propellants (DBP) may have higher energy content than SBP. Their caloric content varies between 3800 and 5200 kJ/kg depending on their type. The grains of DBP are also with different sizes and shapes. They could be compact or porous. The application of DBP for obtaining an adhesive effect in low-explosive mixtures is a possible approach against the stratification of the ingredients, which are with different sizes and weights. The prices of waste SBP and DBP in Bulgaria are around 0.10 BGN/kg.

Experiments

The used secondary propellants were produced in 198 at Arsenal EAD, Bulgaria, and were aged in dry atmosphere without any light.

Fig. 1. General image of DBP type NDT-3 18/1 and SBP type 18/1 (down)

The nitro-glycerine gunpowder (DBP) with the brand name NDT-3 18/1 and the 18/1-branded pyroxyline SBP with long tube-shaped bodies should be further processed by grinding after the extraction from the unnecessary army munitions. The size of propellant grains should be similar to the size of the porous prills of ammonium nitrate as protection against stratification of the ingredients. This implies the development of a facility for safe and effective milling of these brands of gunpowder before their further usage.

Fig. 2. General image of DBP and SBP type after grinding in the mill

For this purpose, a special facility - a mill has been used. After grinding, the grains pass through a 4 mm, 2 mm, 1 mm, 0.8 mm, 0.4 mm and 0.2 mm clear screen. Figure 2 shows the resulting powdery grains after grinding with a particle size of up to 0.2 mm.

Fig. 3. General appearance of the grinding mill for secondary smokeless gunpowder

Three different low-explosive compositions were prepared and loaded in testing cartridges:

- Mixture #1: "flash-powder composition" 65% $KClO_4$ + 35% Al (dark) with Oxygen Balance = -1.12%;

- Mixture #2: 80% gridded DBP + 20% NH_4NO_3 prills with Oxygen Balance = -7.92%;

- Mixture #3: 70% gridded SBP + 25% NH_4NO_3 + 5% Al (dark) with Oxygen Balance = -5.19%;

The ready compositions were loaded in aluminium testing tubes, plugged from the both sides, with the following dimensions:

- 320 mm /ф10 mm inner diameter/ 1 mm wall thickness;
- 320 mm /ф20 mm inner diameter/ 1 mm wall thickness.

Each pipe has three drill holes: first for electric ignition, second for sensor #1 (located at 3 cm from the first hole) and third for sensor #2 (located at 25 cm from the second hole). The ignition of the samples was made by using regular commercial electric "bridge-wire" igniters with smooth burning fuse-head for fireworks and professional pyrotechnic purposes, manufactured by "META PYRO" s.r.o., Czech Rep.

Fig. 4. Loaded and plugged aluminium pipes with el. igniter – ready for test samples

The deflagration velocity was measured by two different devices:

- the "Trio Chronos" apparatus, manufactured by "TRIO Electronics" Ltd., Republic of Serbia, using optic fibre sensors;

Fig. 5. Apparatus for measurement of VOD optical sensors

- the "CNT-66 Pendulum" apparatus, manufactured by "BRL Test" Inc., USA, using a contact wire impact sensor.

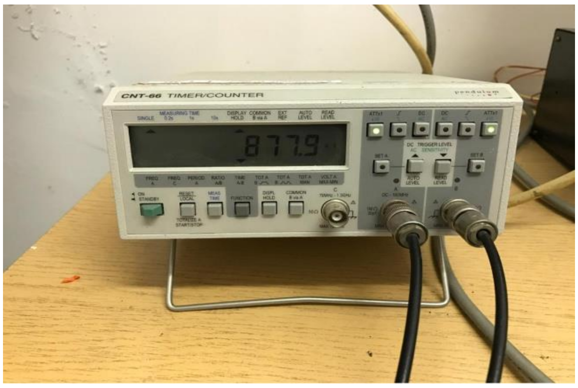

Fig. 6. Apparatus for measurement of VOD with an impact sensor

Sensors and an electric starter were connected to the testing equipment. All laboratory experiments were conducted at the laboratory testing area of "Minproekt", Dragichevo.

After open-air laboratory experiments, a field test at the stone quarry was carried out.

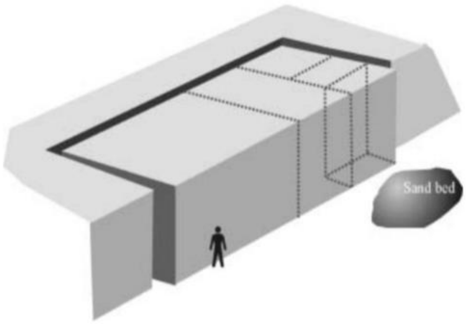

Fig. 7. Principal schedule for extraction of rock-cladding materials – from primary blocks to smaller sized slices, which will be further divided to commercial blocks

Results and discussion

The results from testing of the deflagration velocity of different samples are given in Table 1.

Table 1. *Results from testing of the deflagration velocity of different samples*

Sample №	Inner diameter of the testing tube [mm]	Type of mixture	Velocity of reaction [m/sec.]
1	10	#1	224.46
2	10	#1	7.42
3	10	#1	637.59
4	10	#2	182.23
5	10	#2	251.46
6	10	#2	190.12
7	10	#3	208.67
8	10	#3	334.44
9	10	#3	267.16
10	20	#1	531.32
11	20	#1	1847.70
12	20	#1	897.37
13	20	#2	451.45
14	20	#2	390.08
15	20	#2	407.92
16	20	#3	536.88
17	20	#3	467.14
18	20	#3	537.89

It is visible from the results that Mixture #1 (flash-powder) gives higher velocities of explosive decomposition and because of thein bigger diameters of the charges it is prone to pass from combustion to detonation, which is not suitable to the industrial requirements for low-explosive charges. Mixture #2 (with SBP) and Mixture #3 (with DBP) are increasing their velocities of deflagration with enlarging the diameter of the charge, but the samples containing DBP and Aluminium are releasing more energy, as expected.

An approach for exploiting the flash powder energy (Mixture #1) without a risk of transition from deflagration to detonation was invented for the field tests at the stone quarry. It is well known, that the main reasons for this transition are the high temperature, the high pressure and the big volume of the charge. Small amounts of flash powder (4 g.), accommodated in well plugged paper tubes with a tiny hole, were separately used for the preparation of pyrotechnic petards with zero-delay. Ready petards were applied for the creation of decoupled chain charges with different gaps (air-spacing), by fixing them to a wooden stick and connecting them with a quick fuse. Thus, very low concentrations of the explosive charge in the drill-holes (between 0.040 and 0.065 kg/m) were achieved. Hard casing of the petards and air-gaps between adjacent charges, as well as air-gaps between the charges and the walls of the bore-hole do allow the so-called “flash over”, nor increasing of the pressure to dangerous rates for the transition to detonation. Reliable inert stemming from the top charge to the mouth of the blast-hole assured the necessary conditions for enough pressure of gaseous products, which ensures the needed crack in the desired plane.

Fig. 8. Field test with decoupled chain-charges for smooth splitting at stone quarry

These de-concentrated chain-charges become suitable for really smooth blast-splitting of thin stone slabs, preventing the risk of undesirable fractures and micro-cracks in the material. For successful blast-cutting without undesirable losses of expensive stone material, a very important condition for at least four free surfaces should be accomplished. Otherwise, some curvatures in the direction of the planned crevices could be expected.

Fig. 9. Effect after experimental cautious blast-splitting of stone slice with divided chain-charges

For the field tests at the stone quarry, mixtures #2 and #3 were used for the preparation of 100 g charges in thin plastic bags, fitted to the diameter of drilled holes. The length of the blast holes was 1.60 m. For better distribution of the energy of compressed gases, the explosive charge was separated in two parts with inert stemming between them and simultaneous ignition.

Fig. 10. Ready for loading charges of propellant-based non-detonating compositions

The initial impulse of each charge was provided by fast-speed-deflagrating pyrotechnic booster for better performance of the propellant mixtures. A single petard, containing 4 grams flash composition (Mixture #1) with an electric igniter, was a good solution for that "pyro-booster". The weight of the bottom charge was 0.200kg. The second charge, located in the middle of the hole's length contained 0.100 kg mixture. The total explosive quantity in each blast-hole was 0.300kg propellant mixture. Reliable inert stemming between the charges and especially from the second charge to the mouth of the blast-hole assured the necessary conditions for enough pressure of gaseous products. That guarantees the best possible crack formation for splitting. In order to achieve smoother and more even cracks in the necessary cut-planes, the spacing and collaterality between the drill-holes should be very precise.

Fig. 11. Results after the experimental blasting with propellant-based non-detonating compositions (Mixtures #2 and #3)

The price of the applied materials was 0.6 BGN for the production of one testing cartridge.

Conclusion

The application of waste SBP and DBP after utilisation of old and unnecessary ammunitions is studied for obtaining non-detonating explosive cartridges, suitable in dimension stone mining, as well as for blasting activities in tender and complicated conditions. The velocities of propagation of the reaction of chemical destruction of the tested three different high-energetic compositions were between 180 and 600 m/sec. depending on the diameter of the charges and the ingredients. The propellant based samples did not show any tendency for transition from deflagration to detonation in case of ignition with a soft burning electric fuse-head. The results from the blast-splitting tests in a stone quarry were satisfactory. There were no undesired cracks in the treated rock bodies. No fumes emission, air-blast or fly-rocks were detected after the explosion of propellant-based compositions #2 and #3. The flash-powder (Mixture #1) showed higher velocities of deflagration and because of the bigger diameters of the charges it is prone to pass from combustion to detonation, which makes it useful only for "mini-pyro-boosters" or multi-deck charges from chained small diameter petards.

Acknowledgements. Cordial thanks to the management and employees at the laboratory of "MINPROEKT", Dragichevo and "RIOLIT-B", Plovdiv for the provided sites, workers and equipment during the laboratory and field experiments of the samples.

References

Bozhilov, N. 2018. *Proizvodstvo na vodosadarzhashti promishleni eksplozivi, sensibilizirani s bezdimni baruti, polucheni ot utilizaciyata na nenuzhni boepripasi.* PhD Thesis (in Bulgarian).

Mitkov, V. 2007. *Proizvodstvo na eksplozivi za grazhdanski tseli* (in Bulgarian).

Mitkov, V. 2010. *Bezopasnost pri proizvodstvoto I upotrebata na eksplozivi* (in Bulgarian).

Shishkov, P., N. Stoycheva. 2018. Savremenni vzrivni tehniki za dobiv na skalno-oblicovachni materiali. − *Mining and Geology Magazine*, 10−11, 42−49 (in Bulgarian with English abstract).