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Rock splitting with pyrotechnic compositions and secondary propellants

Petar Shishkov[1*], *Nadezhda* Stoycheva[2], and *Vladimir* Penev[1]

[1]University of Mining and Geology “St. Ivan Rilski”, Department “Underground construction”, 1, Prof. Boyan Kamenov str., Studentski grad district, Sofia, Bulgaria
[2]University of Mining and Geology “St. Ivan Rilski”, Department “Development of Mineral Resourses”, 1, Prof. Boyan Kamenov str., Studentski grad district, Sofia, Bulgaria

Abstract. In some cases of resources extraction, as well as in construction at industrial and urbanized territories, commercial explosives are not safe enough for the surroundings 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 the mechanism of the chemical reaction of explosive decomposition. The authors shifted the focus of their researches from detonating explosives to high-speed combusting energetic materials. The production of low explosive non-detonating mixtures from long-term stored smokeless gunpowders and ammonium nitrate prills in different configurations, and popular pyrolant compositions were studied. The samples of different cartridge casings, filled with non-detonating propellant mixtures or pyrotechnic compositions were examined by two methods - for velocity of propagation and by field tests. It was made investigations for application of waste single-base-powders and double-base-powders for obtaining non-detonating explosive cartridges, suitable in dimension stone mining, as well as in blasting activities at tender and complicated conditions.

1 Introduction

1.1 About explosive chemical decomposition

The velocity of detonation (VoD) is the rate at which the detonation wave travels through the explosive charge [1]. The higher this velocity, the greater the "force" or the crushing effect of the explosive. Higher velocity explosives are better suited for blasting in hard rocks, and low-velocity explosives are appropriate for work in soft and cracked rocks [2]. In general, "low-speed" explosives tend to release gaseous products for a relatively longer period, and therefore exhibit better heaving effect. Detonation rates of different industrial explosives range between 2500-7500 m/sec. Detonation pressure is the pressure in the

* Corresponding author: peter.shishkov@mgu.bg ; sfxman86@yahoo.com

reaction zone when explosive molecules break down. The later is an important indicator of the explosive's ability to induce a good fragmentation [3,4].

Deflagration is a subsonic reaction of chemical decomposition of the explosives. It is typical for propellants and pyrolants, which could act on the solid medium by the pressure generated by gaseous products from chemical reaction. There is practically no shock energy generation. In reality, such an effect occurs when a charge of blasting gunpowder is ignited in an appropriately tamped blast hole [1,2].

1.2 About pyrotechnic compositions

In accordance with definition by Boychev Y. & Asenov S. in [5], pyrotechnic compositions are a substance or mixture of substances intended to produce special effects - heat, light, sound, smoke, gas, or a combination thereof, as a result of spontaneous exothermic red-ox reactions that do not require oxygen from external sources. The main ingredients are oxidizer and fuel (reducer). Various additional modifiers could be present in the mixtures, regarding needed effect [6]. Depending on the speed of the chemical reaction, several different forms of chemical conversion could occur – thermal decomposition, burning mode, combustion, deflagration, atypical detonation and detonation. The factors that determine which form would develop are:

- chemical nature of the components;
- degree of dispersion;
- homogeneity of the mixtures;
- presence of impurities, especially moisture;
- type and power of the initiating pulse;
- location of application of the initiating pulse in the volume of the charge;
- quantity of the bulk mixture;
- density of the composition;
- degree of the confinement of the mixture;
- construction of the pyrotechnical device [7].

High-performance propellants, imitation mixtures, photo mixtures, and so called "flash powders" are types of pyrotechnic compositions which are suitable for achieving a gas-generating high-temperature effect in a time range of milliseconds.

In 1992, Kuwahara T. and Ochiai T. introduced in [8] the term "pyrolants". These are materials, typically including metallic or non-metallic fuels (Al, Mg, Ti, Si, B, S) and inorganic [$Ba(NO_3)_2$, $NaNO_3$, $KClO_4$] and organic [C_2Cl_6, $(C_2F_4)n$] oxidants, in the combustion of which emit bright light and condensed products (hot gases). They are characterized by a high enthalpy of combustion (1-30 kJ/g) and a density in the range of 2-10 g/cm^3.

1.3 About waste smokeless gunpowders

It is well known, that single based propellants (SBP) generally are pelletized or extruded porous grains in different sizes and shapes, which usually contains 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. Double-based propellants (DBP) are mixtures of nitrocellulose (NC), 2-8 % additives (similar to these in SBP) and nitro-esters, usually nitroglycerin (NG). The content of NG is about 10 - 38 %. The boiling point of NG is 50 ºC. DBP might have higher energy content than SBP. Their caloric content varies depending on their types between 3800 and 5200 kJ/kg. The grains of DBP are also with different sizes and shapes.

They could be compact or porous regarding the type. The prices of waste SBP and DBP in Bulgaria are around 0,10 EUR/kg [9].

The authors focused their researches to laboratory experiments for combustion rates and field tests for explosive performances of high-speed combusting energetic materials on the base of pyrotechnic compositions and secondary propellants.

2 Experimental setup

The propellants, investigated in this study are nitroglycerine gunpowder (further referred to as DBP) with the brand name NDT-3 18/1 and the 18/1-branded pyroxylin SBP. The test specimens are in form of long tube-shaped bodies, and are further processed by grinding after their extraction from decommissioned ammunitions. The size of propellant grains should be similar to the size of the porous prills of ammonium nitrate as prevention against stratification of the ingredients. Three different compositions were designed and mixed for further research at the laboratory testing field, at a stone quarry.

Mixture №1: "flash-powder composition" 45% KNO_3 + 20% $KClO_4$ + 35% Al (dark);
Mixture №2: 55% grinded SBP + 45% NH_4NO_3 prills;
Mixture №3: 42% grinded DBP + 55% NH_4NO_3 + 3% Al (dark);

Ready compositions were loaded in aluminum testing tubes, plugged at both sides (Fig. 1) 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 3 drill holes: the first one is for electric ignition, the second one is for sensor №1 (located 3 cm from the first hole) and third for sensor №2 (located 25 cm from the second hole). The ignition of the samples was made 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. 1. Test samples - loaded and plugged aluminium pipes with electric igniter

The velocity of deflagration was measured by two different devices:
- with apparatus "Trio Chronos", manufactured by "TRIO Electronics" Ltd., Rep. of Serbia, using optic fiber sensors.
- with apparatus "CNT-66 Pendulum", manufactured by "BRL Test" Inc., USA, using contact wire impact sensor.

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

3 Results and discussion

The velocity of explosive decomposition for the different samples are given in Table1.

Table 1. Experimental results for velocity of explosive reaction of different samples

Sample №	Inner diameter of the test tube (mm)	Mixture type	Velocity of reaction (m/s)
1	10	№1	240,35
2	10	№1	490,71
3	10	№1	15,54
4	10	№2	210,69
5	10	№2	262,18
6	10	№2	279,42
7	10	№3	313,96
8	10	№3	356,43
9	10	№3	292,18
10	20	№1	718,63
11	20	№1	855,98
12	20	№1	1793,77
13	20	№2	458,41
14	20	№2	501,88
15	20	№2	488,94
16	20	№3	576,42
17	20	№3	530,11
18	20	№3	600,63

The results show that pyrolant Mixture №1 (flash-powder) provides to higher velocities of explosive decomposition and in bigger diameters of the charges is inclined to pass from combustion - to detonation, which is not acceptable to industrial requirements for low-explosive charges. Propellant containing compositions Mixture №2 (with SBP) and Mixture №3 (with DBP) are increasing their velocities of deflagration with enlarging the diameter of the charge, but samples containing DBP and Aluminum are releasing more energy, as expected.

After laboratory experiments, some field tests at the stone quarry were conducted. Few boulders with similar shapes and sizes were selected for testing of blast-splitting capabilities. Regarding the risk of transition from deflagration to the detonation of “flash powder composition” (Mixture #1), small charges of 0,050 kg was poured without compaction in well-plugged paper tubes with inner diameter 25 mm and 150 mm length. The conditions for possible shock wave generation and detonation of that sensitive flash-compositions are higher density, bigger diameters, and larger volumes of the charges. The authors decided to use petards with a smaller diameter than the blast-hole. The existing air gaps between the decoupled charges and the walls of the bore-hole prevent increasing the pressure to dangerous rates for transition from combustion to detonation. Very low concentrations of an explosive charge in the drill-holes between 0,100 kg/m^3 and 0,150 kg/m^3 has to be achieved for split-blasting without undesired crack propagation. This is the reason, in the case of bore holes longer than 1,0 m, multi-deck charges are a better choice for smooth blasting.

All petards were equipped with traditional fuse-head electric igniters, usually applied in professional fireworks events. Each device was protected with water-resistant polymer foil. These electrically controlled low-explosive cartridges were used like bottom charges in single or double parallel blast holes, drilled in stones with volumes between 4 ÷ 6 m^3. The selected rock boulder samples were free standing (with free surfaces) and similar shapes. Proper stemming has a leading role in the quality of the performance of the non-detonating explosives in the blast-splitting activities. When we prefer to deprive from the advantage of the supersonic pressure wave, which causes a sharp impact on the rock, we have to ensure long enough retention of the explosive gases pressure in the drill hole.

Very good results were achieved after treating the boulders with a single charge of the aforementioned petards in a short borehole with a diameter 45 mm and length 0,60 m. A smooth-walled cleft was obtained throughout the volume of the stone. No additional cracks were observed in the area of the blast hole (Fig. 2).

Fig. 2. Splitting of a boulder with one charge of 0,050 kg. Mixture #1 in single blasthole with length 0,60 m.

After the experiments with flash powder composition, further tests with receipts containing secondary smokeless powder were conducted. For the field tests at the stone quarry Mixtures #2 and #3 were used for the preparation of 0,050 kg and 0,100 kg charges in thin plastic bags fitted to the diameter of the drilled holes (Fig. 6). As it is known, smokeless gunpowders have so-called “progressive combustion”, the speed of which depends on the pressure in the burning area, the power of the ignition pulse and the surface of initial ignition. For this reason, the authors preferred to ignite those propellant charges not directly by electric igniters, but with small pyrotechnical “boosters”. 3-4 g of pyrolant Mixture #1 and electric igniter was used for the preparation of each petard, which was intended to provide the boosting energy for massive inflammation of our foil-cartridges with Mixtures #2 and #3. As it is described by Boychev Y. and Asenov S. in *"Non-lethal devices with multi-sensory action"*, during deflagration of flash-mixtures, fine metal particles of the fuel are evaporating and due to the high temperatures and pressure, they transition into a plasma state. Driven by the high pressure of the hot gasses, the sparks and plasma are penetrating deep through the gaps between the bigger grains of the propellant. In this way, several layers are ignited simultaneously in the depth of the charge. The combustion of propellant mixtures starts with a higher initial rate and pressure, which in the conditions of tamped drill-hole contributes to a shorter period of increase of the velocity of the explosive reaction. In practice, a higher deflagration rate means a larger amount of hot gases, emitted per unit of time. This affords better performance of the low-explosive.

New experiments were performed with charges of Mixture #2 (in plastic bags). Pyrotechnical booster was loaded first on the bottom of the 0,60 m deep drill-hole. Plastic "cartridge" with 0,050 kg of the tested composition with a diameter close to the hole size was tightly inserted over the booster. Then, the blasthole was filled with reliable stemming. There was an excellent clean splitting of the stone after a low-noise explosion with a slight displacement of the two parts (Fig. 3).

Fig. 3. Splitting of a boulder with one charge of 50 g Mixture #2 in single blasthole with length 0,60 m.

The last experiment was done for the extraction of a stone block with a volume of almost 8 m^3 by splitting from a rock body with three free faces. Taking into account more complex conditions for explosive influence, the authors preferred to use two longer bore-holes and cartridges from packed in a thin polymer bag Mixture #3. The length of the blast holes was 1,80 m. For better distribution of the energy of compressed gases, the explosive charge was separated into two parts with inert stemming between them and simultaneous ignition. Two handmade cartridges weighing 0,100 kg each with one electrically ignited pyro-booster were placed for bottom charge in every hole. They were well sealed with 30 cm semidry sandy-clay stemming. One pyro-booster, equipped with electric igniter and single cartridge of 0,100 kg Mixture #3 was used for the second decked charge in the blast-holes. The total explosive quantity of each blast-hole was 0,300 kg propellant mixture. Reliable inert stemming between charges and especially over the second charge to the mouth of the blast-hole assured so desirable condition for enough pressure of gaseous products. That guarantees as better as possible crack formation for splitting.

Although all measures have been taken to avoid detonation when using propellant composition, the combination of high-speed deflagration with too large volume of gases (generated by preloaded bottom charges) caused an unnecessary throwing effect and several additional cracks in unexpected directions (Fig. 4). This was a sign that a more precise calculation of the parameters of drilling and blasting was needed.

Fig. 4. Splitting of rock body with two parallel boreholes. Effects from preloaded bottom charge of 300 g. Mixture #3 and decked second charge of 150 g. Mixture #3 in every single blasthole with length 1,80 m.

4 Conclusions

Researches for application of waste SBP and DBP after utilization of decommissioned ammunitions for obtaining of non-detonating explosive cartridges, suitable for dimension stone mining, as well as for blasting activities at challenging and complex conditions. The velocities of propagation of the reaction of chemical destruction of tested 3 different high-energetic compositions were between 210 and 718 m/s depending on the diameter of the charges and ingredients.

Propellant-based samples do not show any tendency for transition from combustion to detonation in case of ignition with soft burning electric fuse-head.

Pyrolant Mixture #1 shows higher velocities of deflagration and in bigger diameters of the charges is inclined to pass from combustion to detonation, which makes it useful mainly for decoupled charges, “mini-pyro-boosters” or multi-deck charges from chained petards with small diameter, separated with air gaps.

In case of splitting with multiple blast-holes in a row, for achieving more smooth and equable cracks in necessary cut-planes, the spacing and collateral between drill-holes should be précised.

Despite the fact, that explosive is not detonating, a preloaded blasthole could cause some rupture damages or overbreaks around the charged area.

In-situ experiments for application of fast combusting pyrotechnic composition for blast-swelling of concrete in the volume of the mixer have shown satisfactory results – good fragmentation and absence of damages on the mixing barrel. There was no fumes emission, air-blast or fly-rocks after explosion of pyrolant composition.

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