ГЕОМЕХАНИКА. РАЗРУШЕНИЕ ГОРНЫХ ПОРОД

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Frost-resistant emulsion explosives

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Abstract
Introduction. *The paper considers the development of a frost-resistant emulsion explosive (EE) to create cartridges, including the ones with a small diameter.*
Research objective *is to develop a frost-resistant cap-sensitive EE to create cartridges, including the ones with a small diameter, to increase the reliability, efficiency, and safety of blasting operations in the northern and Arctic regions.*
Methods of research *are based on EE frost resistance theoretical analysis and laboratory study, as well as ground tests on detonation velocity and completeness in the developed EE.*
Results. *It is shown that EE with an oxidizing phase based on a binary solution of ammonium and calcium nitrate with calcium chloride under a particular water content and with a fuel phase based on the DEP-1 emulsifier solution in a wide range of petroleum products meets the requirements of frost resistance. The resulting EE in a practically relevant temperature range (–60…+40 °C) represents an elastoplastic body that makes it possible to form durable cartridges that retain geometry. The socket for the detonator capsule is easily made anywhere in the cartridge using aluminum piercel or drill of the wood twist drill type. EE reliably detonates from the detonator capsule of the non-electric detonation system (SINV). The detonation velocity in open cartridges 32 mm in diameter is 4700–5000 m/s.*
Conclusions. *The results obtained in the article justify the development of EE compositions suitable for patronized explosives for the northern and Arctic regions.*

Keywords: *northern regions; Arctic regions; emulsion explosive; crystalline hydrates; frost resistance; cartridged EE.*

Relevance. Russian mineral resource base is expanded by large-scale development of rich solid mineral deposits in hard-to-reach and uninhabited areas of the Polar Urals, Eastern Siberia and the Far East. Up to 40% of gold reserves and almost 100% of primary diamond deposits are in the Russia's Arctic zone alone [1]. The extraction of materials and the inevitable construction of buildings, structures, roads, airfields, ports, etc. require higher consumption of industrial explosives. It is therefore absolutely essential to develop technologies for efficient blasting in severe climatic and complex mining and geological conditions.

The basis of any blasting technology is the explosive.

Emulsion explosives (EE) have recently got widespread in Russian mining industry [2]. However, severe climatic conditions and deposits remoteness made some researchers assume that, when developing Russia's northern and Arctic regions, it is advisable to focus on simplest explosives and their application technologies instead of focusing on emulsion explosives [1–6]. The following statements support this argument [1]:

– emulsion explosives production in the conditions of the North of Russia is unprofitable due to the high cost of energy;

– regular explosives are not practical due to expensive logistics and lack of high-capacity storage facilities for explosives in remote regions.

However, mass transition to the simplest explosives in Russia's northern and Arctic regions is hampered by the following factors:

– the solubility of ammonium nitrate, the main mass component of the simplest explosives, which greatly complicates blasting in unfrozen and watered ground (rocks);

– the demand for cartridged water-resistant and frost-resistant explosives caused by the prevalence of shallow-hole blasting in the extraction of valuable non-ferrous metal ore, as well as in the underwater and coastal blasting operations and ice blockage removal.

It should be noted that the development of EE production and application technology has shown the possibility of their effective use for ore extraction in remote deposits located in severe climatic conditions. It turned out that it is possible to produce matrix emulsion at a considerable distance from the places where EE are used, and it can be delivered there in corrugated cardboard containers [7]. Along with the developed methods of cold emulsion sensitization [7, 8], it allows to use EE at some remote deposits located in the north-east of the country.

However, the demonstrated achievements keep from omitting regular cartridged explosives. Therefore, the development of a frost-resistant EE to create cartridges, including the ones with a small diameter, is an urgent task for the northern and Arctic regions development.

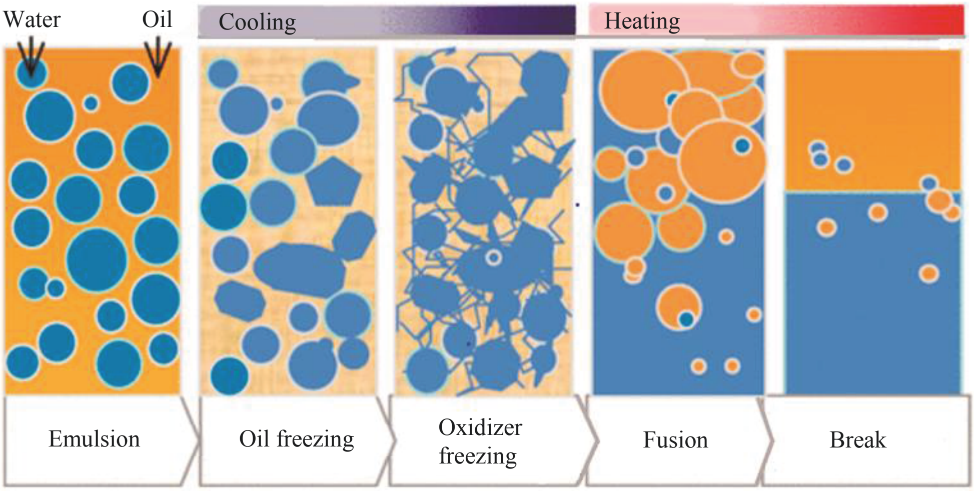

Figure 1. Inverse emulsion break under the "freeze–thaw" processes [9]
Рисунок 1. Разрушение обратной эмульсии при процессах «замерзание–оттаивание» [9]

Research results. EE for Arctic conditions should be thermal cycling resistant. An analysis of research on inverse emulsion resistance to "freeze–thaw" processes shows that emulsion is resistant if its fuel phase does not freeze until water freezes in droplets of the oxidizing phase [9–15].

Figure 1 shows the processes that occur when the emulsion freezes. If the fuel phase is the first to freeze, it will be damaged by the subsequently freezing oxidizing phase expansion. As a result, a certain amount of the liquid oxidizing phase is drawn into the small cracks of the frozen fuel phase. These processes result in emulsion break in the course of thawing, inevitably leading to the loss of EE detonability.

To solve this problem, it is proposed to use EE with an oxidizing phase based on a binary solution of ammonium and calcium nitrate.

It is known that calcium nitrate forms several stable and unstable crystalline hydrates. Stable calcium nitrate crystalline hydrates exist within the following temperature ranges [16]:

– under 51.1 °C ≤ *t* stable hydrates are not formed;

– under 42.7 °C ≤ *t* ≤ 51.1 °C calcium nitrate trihydrate is formed;

– under *t* ≤ 42.7 °C calcium nitrate tetrahydrate is formed,

where *t* is the emulsion temperature, °C.

So, under the emulsion temperature below 51.1 °C, water in EE is combined into calcium nitrate trihydrate, and into calcium nitrate tetrahydrate under the emulsion temperature below 42.7 °C, which leads to a reduced content of free water in EE. Decreased free water content reduces the probability of damaging the oil film that envelops the emulsion oxidizing phase particles, when the oil film is cooled down below the freezing point of the oxidizing phase due to the increased volume of these particles.

In Arctic conditions it is proposed to use the EE the matrix emulsion of which has a composition characterized by the dependence between the water content in the emulsion and the content of calcium nitrate and calcium chloride:

$$M_{H_2O} = \mu_{H_2O}\left(\frac{N_{Ca(NO_3)_2} M_{Ca(NO_3)_2}}{\mu_{Ca(NO_3)_2}} + \frac{N_{CaCl_2} M_{CaCl_2}}{\mu_{CaCl_2}}\right), \quad (1)$$

where $\mu_{H_2O} = 18$; $\mu_{Ca(NO_3)_2} = 164$; $\mu_{CaCl_2} = 111$ are the molecular masses of water, calcium nitrate, and calcium chloride, respectively, g/mol; $N_{Ca(NO_3)_2}$, N_{CaCl_2} is the number of water molecules in the hydrate combined with the molecule of the hydrate-forming substance; M_{H_2O}, $M_{Ca(NO_3)_2}$, M_{CaCl_2} are the fractions of water, calcium nitrate and calcium chloride in the emulsion, respectively, wt%.

If condition (1) is fulfilled, under emulsion cooling, water will be in a crystalline hydrate state only. It will provide the emulsion with substantial resistance to "freeze–thaw" processes. It can be shown that the maximum possible amount of water in the emulsion, which can be in the crystalline state at temperatures below +40 °C, is reached under $N_{Ca(NO_3)_2} = 4$; $N_{CaCl_2} = 4$. However, for reliable formation of crystalline hydrates, it is advisable to reduce the amount of water in the emulsion oxidizing phase, therefore, to calculate the amount of water in the emulsion, the following was assumed: $N_{Ca(NO_3)_2} = 3$ and $N_{CaCl_2} = 4$.

So, substituting numerical values into equation (1), we get:

$$[H_2O] = 0{,}3293[Ca(NO_3)_2] + 0{,}6486[CaCl_2], \quad (2)$$

where $[H_2O]$, $[Ca(NO_3)_2]$, $[CaCl_2]$ is the content of water, calcium nitrate and calcium chloride in the emulsion matrix, respectively, wt%.

The use of calcium chloride is due to its ability to form crystalline hydrates [17]:

– at temperatures below 50 °C, calcium chloride dihydrate, which exists at temperatures above 50 °C, turns into a tetrahydrate;

– at temperature below 29.2 ° C it turns into the hexahydrate.

This allows to combine in hydrates a certain amount of water that entered the reactor in excess of the calculated amount. Calcium chloride also makes it possible to expand the acceptance region for the content of calcium nitrate, at which it is possible to synthesize effective EE that do not have free water in the emulsion at temperatures below 50 °C.

The proposed composition of EE contains only 8.0–10.0% wt% of water. It can cause rapid crystallization of the supersaturated saline solution in the emulsion. Experiments have shown that resistance to crystallization is reliable if 20% solution of the DEP-1 polymer dispersant-emulsifier is used as the fuel phase in petroleum products.

DEP-1 (TU 20.41.20-002-73592474-2022 [18]) is a polymeric surfactant based on amine derivatives of polyisobutylene succinic anhydride (PIBSA).

The proposed compositions were prepared as follows: sample weights of calcium nitrate and calcium chloride were dissolved in the estimated amount of water at a temperature of 120 °C. After that, the required amount of ammonium nitrate was added to the solution and the temperature was raised to 90–95 °C, the solution was continuously stirred. In a different container, the fuel phase of the emulsion matrix was obtained by preparing a 20% solution of the DEP-1 emulsifier in mineral oil at a temperature of 50–60°C. Oxidizer solution was continuously added into the resulting fuel phase under rapid stirring (1500–2000 rpm). The mixing time was 90–120 s. The ratio of the oxidizing and fuel phases of these compositions was selected to ensure an oxygen balance close to zero.

Table 1. Emulsion explosive compositions for northern and Arctic regions and their detonation properties under complete detonation of EE

Таблица 1. Составы эмульсионного взрывчатого вещества для применения в северных и арктических регионах и их детонационные свойства при полной детонации ЭВВ

Component	Composition number, wt%				
	1	2	3	4	5
Ammonium nitrate	53.2	60.1	64.39	62.5	58.85
Calcium nitrate	28.4	20.0	16.41	17.6	25.0
Calcium chloride	1.0	3.7	4.0	4.0	0.25
Fuel phase: DEP-1 emulsifier + industrial oil	7.4	7.2	7.2	7.5	7.5
Water	10.0	9.0	8.0	8.4	8.4
EE density, g/cm^3	1.177	1.166	1.161	1.161	1.171
Detonation velocity, m/c	4670–4900	4670–4920	4740–5040	4750–5030	4780–5070

The detonation properties were determined by the completeness of detonation of an open charge 32 mm in diameter when it was initiated by the detonator capsule of the non-electric detonation system (SINV). Additionally, the detonation velocity was measured in polyethylene pipes with an inner diameter of 40 mm. Sensitization was carried out with glass microspheres about 80 μm in diameter. Emulsion particles size was 2.5 μm.

Information on EE compositions and test results is given in Table 1. Experiments demonstrated that the proposed EE compositions can be obtained using various liquid hydrocarbons (diesel fuel, industrial mineral oils I-10, I-20, I-40 and their mixtures).

The resulting EE in a relevant temperature range (–60…+40 °C) represents an elastoplastic body that makes it possible to form durable cartridges that retain geometry. The socket for the detonator capsule is easily made anywhere in the cartridge using aluminum piercel or drill of the wood twist drill type.

Further increase in the content of calcium nitrate and a decrease in the amount of water results in reduced emulsion stability, which is technologically and economically impractical.

Conclusions. Blasting technology analysis shows that the development of frost-resistant EE for cartridges, including the ones with a small diameter, is an urgent task.

The present research shows that EE with an oxidizing phase based on a binary solution of ammonium and calcium nitrate with the addition of calcium chloride under a water content of $[H_2O] = 0,3293[Ca(NO_3)_2] + 0,6486[CaCl_2]$ and with a fuel phase from the DEP-1 emulsifier solution in a wide range of petroleum products $[H_2O]$, $[Ca(NO_3)_2]$, $[CaCl_2]$ meets the requirements.

The resulting EE in a relevant temperature range (–60…+40 °C) represents an elastoplastic body that makes it possible to form durable cartridges that retain geometry. The socket for the detonator capsule is easily made anywhere in the cartridge using aluminum piercel or drill of the wood twist drill type.

EE reliably detonates from the detonator capsule of the non-electric detonation system (SINV). The detonation velocity in open cartridges 32 mm in diameter is 4700–5000 m/s.

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Морозоустойчивые эмульсионные взрывчатые вещества

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Реферат

Введение. *Рассмотрены вопросы, связанные с разработкой морозоустойчивого эмульсионного взрывчатого вещества (ЭВВ) для создания патронов, в том числе и малого диаметра.*

Цель работы. *Разработать морозоустойчивое капсюлечувствительное ЭВВ для создания патронов, в том числе малого диаметра, для повышения надежности, эффективности и безопасности взрывных работ в северных и арктических регионах.*

Методология. *В основу методики исследований положены теоретический анализ и лабораторное изучение морозостойкости ЭВВ, а также полигонные опыты по изучению полноты и скорости детонации.*

Результаты. *Показано, что требованиям морозоустойчивости удовлетворяет ЭВВ с окислительной фазой на основе бинарного раствора аммиачной и кальциевой селитр с добавкой хлористого кальция при определенном содержании воды и с топливной фазой из раствора эмульгатора «ДЭП-1» в широком спектре нефтепродуктов. Получаемое ЭВВ в практически значимом диапазоне температур (–60…+40 °С) представляет собой упруго-пластичное тело, позволяющее формировать прочные, сохраняющие свои геометрические размеры патроны. Гнездо для размещения капсюля-детонатора легко делается в любом месте патрона при помощи алюминиевого шила или сверла типа «спиральное для древесины». ЭВВ надежно детонирует от капсюля-детонатора СИНВ (неэлектрическая система инициирования взрыва). Скорость детонации в открытых патронах диаметром 32 мм составляет 4700–5000 м/с.*

Выводы. *Полученные в статье результаты служат основанием для разработки составов ЭВВ, пригодных для создания патронированных взрывчатых веществ для северных и арктических регионов.*

Ключевые слова: *северные регионы; арктические регионы; эмульсионное взрывчатое вещество; кристаллогидраты; морозостойкость; патронированное ЭВВ.*

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