

UDC 661.52:662.2+622.235.433

I.L. Kovalenko, Ph.D., Assoc.Prof.,
V.P. Kuprin, Doctor of Chemistry, Professor,
Ukrainian State University of Chemical Engineering
(Dnipropetrovsk)

ENERGY CONDENSED PACKAGED SYSTEMS. OXIDIZER COMPONENTS SELECTION

Introduction. Ammonium nitrate represents the most large-capacity product of nitric industry, widely used as a fertilizer and as an oxidant at energy condensed systems (ECS), including industrial emulsion explosives (IEE) for the mining industry.

The experience of emulsion explosives' use to break rocks shows that these systems are as effective as TNT explosives, but have much efficiency and significantly higher safety level at the same time that their explosion products are more environment-friendly.

Literature review. Well known is [1...3] that the IEE do represent highly concentrated inverse emulsions of nitrate salts' water melts in the fuel phase, sensitized with microspheres or gas bubbles. It has been found that most of IEE properties are determined by emulsion dispersion, which increases concurrently to increase of "oxidizer — fuel" boundary surface that provides the system's high sensitivity and detonation characteristics [1...3]. However, dispersion increasing the system failure thermodynamic probability also does increase.

ECS emulsion base preparation consists in emulsification of inorganic oxidizing salts' highly concentrated water melts (85...90 %) in fuel phase. However, when IEE application temperatures (10...70 °C), the emulsion dispersed phase represents a supersaturated solution that creates salts crystallization and emulsion breaking conditions, and, consequently, involves the ECS detonation capacity loss.

Aim of the Research. To obtain a stable high-dispersion emulsion through well-argued selection of the nature and concentration of the oxidizer phase, fuel phase and emulsifier, as well as the emulsification method.

Main Body. The modern emulsion explosives do use as an oxidant the ammonium nitrate (NH_4NO_3) sodium (NaNO_3) and calcium nitrates ($\text{Ca}(\text{NO}_3)_2$). Calculations show that by the excessive oxygen index determined by the so-called oxygen balance (OB) [3], the calcium (OB=48,8 %) and sodium (OB=47 %) nitrates are significantly superior over the ammonium nitrate (OB=20,0 %). Thus, to obtain a balanced redox system used as oxidant for sodium and calcium nitrates we must increase the emulsion content in fuel phase that allows a greater thermal expansion of the ECS explosive effect. However, the total replacement of emulsion's ammonium nitrate with the calcium or sodium nitrates is not effective as under thermal decomposition these nitrates do form solid products that reduces the amount of gases released by IE explosion and respectively blast effect [4]. At the same time, using only ammonium nitrate (AN) as an emulsion systems' oxidant requires maintaining high process temperatures when IEE manufacturing.

As ECS component, the water represents a salts' solvent and the base to form a dispersed fluid system that provides producing an IEE convenient for pumping into the well with high throughput. The water content in such emulsion depends on the IEE application and type [1, 2]. For liquid emulsion systems purposed for both open and underground mining, the water content is within range of 14...18 % by weight. Case of packaged systems used for underground works, crushing of oversize mining product or when used as a detonator cartridge, the water content is limited to 6...9 wt.%, that is explained by water peculiarities as a system component.

Water increases the energy condensing system density and, forming an incompressible liquid phase, maintains a high detonation velocity. Increasing the water content makes the emulsion system

DOI 10.15276/opu.2.44.2014.32

© I.L. Kovalenko, V.P. Kuprin, 2014

safer by reducing its sensitivity to impact, friction, sparks, etc. However, the chemical inertness and the explosion energy losses for water evaporation do lead to a decrease in IEE explosion efficiency: the ECS water content 1 wt.% increase results in the explosive system efficiency decrease of 1,7 % [5].

Thus, the optimum water content and oxidant composition are major issues for controllable properties ECS emulsion technologies.

Results. Fig. 1 shows the crystallization onset temperature (t_{cr}) for binary oxidizers' solutions with water content of 17 wt.%, that corresponds to the emulsion water content of 15...16 wt.%. The t_{cr} values are established in accordance with GOST 18995/5-73.

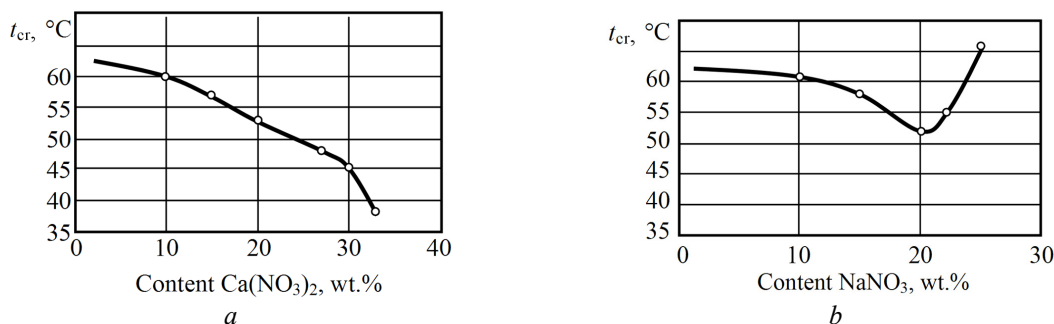


Fig. 1. Crystallization onset temperature for systems " $\text{Ca}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$ " (a) and " $\text{NaNO}_3 - \text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$ " (b), with water weight content of 17 %.

As we can see from Fig. 1 the $\text{Ca}(\text{NO}_3)_2$ adding to the NH_4NO_3 solution involves a continuous decrease in t_{cr} , as opposite to NaNO_3 , in which case we observe an extreme increase in t_{cr} when the sodium nitrate content exceeds 20 % by weight. Such dependency can be explained by low solubility of NaNO_3 compared to $\text{Ca}(\text{NO}_3)_2$, which effect finds a specific feature expressed with ionic hydration energy: Na^+ ($\Delta G = -824,4 \text{ kJ/mol}$) and Ca^{2+} ($\Delta G = -2405,0 \text{ kJ/mol}$) [6].

Thus, to reduce the liquid IEE oxidizing solution t_{cr} we can use both $\text{Ca}(\text{NO}_3)_2$, and NaNO_3 (in an amount never exceeding 20 wt.%). However, when transition to packaged ECS, which should have improved detonation properties, achieved mainly due to lower water content, use of NaNO_3 is impractical due to its low solubility (176 g in 100 g water at 100 °C).

Thus, it is necessary to study the solubility of " $\text{Ca}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3$ " system at water content of 6,0...10,0 wt.%. Considering that the dispersed phase (melt nitrates) concentration in the emulsion systems' composition is within 90...92 wt.%, we determined the crystallization onset temperature for calcium and ammonium nitrates' binary solutions containing 6,6...9,9 wt.% of water, that corresponds to a water content of 6...9 wt.% for an emulsion with dispersed phase concentration of 91,0 wt.% (Fig. 2).

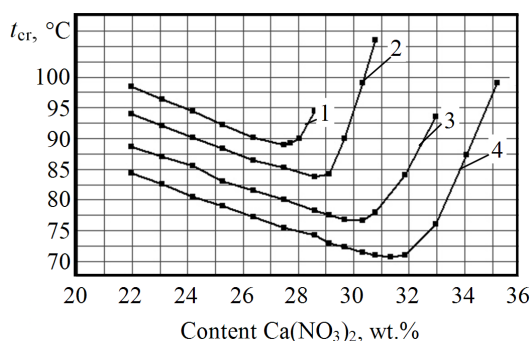


Fig. 2. Crystallization onset temperature for systems " $\text{Ca}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$ " with water weight content of: 1 — 6,6; 2 — 7,7; 3 — 8,8; 4 — 9,9

As evidently shown at Fig. 2 when the solution's water content is below 10 wt.% the t_{cr} dependence upon $\text{Ca}(\text{NO}_3)_2$ content is extremely specific.

In such a way the basic oxidizing solution for packaged emulsion system should have the following composition, % by weight: H_2O 7,0...10,0; $\text{Ca}(\text{NO}_3)_2$ 27,5...31,5; NH_4NO_3 58,5...65,5.

Emulsions obtained using the specified composition of the oxidant (91 wt.%) and emulsifier "Ukrainit-M" (TU U 20.5-1943711-002: 2012) in the amount of 9 % by weight, have high stability and resistance to crystallization, as evidenced by X-ray diffraction data and optical measurements [3].

One of the key requirements to packaged IEEs, along with high stability, consists in stable detonation

of small diameters (32 mm or less) that allows charging such ECS packs in holes when underground mining. In this connection of a special interest would be to clarify the effect onto the IEE critical detonation diameter, sensitivity and detonation characteristics, when introducing calcium nitrate in the oxidizer.

The source [7] does suggest an approximation model for the description of energy-condensing emulsion systems' detonation decomposition based on two-polytropic approximation by L.D. Landau, K.P. Stanyukovich [4]. The model allows calculating the ECS main detonation characteristics: ideal detonation velocity (D), critical diameter of detonation (d_{crit}), relative efficiency (f) etc, depending on the components' composition and chemical nature, as well as on the IEE porosity. Since the ECS emulsion base is insensitive to any initiating impulse, it is sensitized due to "gas-filling" the hollow microspheres or gas bubbles. When calculation we does mean the porosity as a parameter defined with volume fraction of IEE gas inclusions.

Fig. 3 represents the calculated data of the detonation velocity dependence from the mass fraction of nitrate, replacing the ammonium nitrate as IEE component [8].

From Fig. 3 we observe that the speed of the detonation process propagation at IEE based on the ammonium nitrate monosolution, given the consideration systems have same structure, is always higher than at IEE with the oxidant binary composition. The same applies to the performance of emulsions (Table 1) within porosity range of practical interest [9].

Calculated values of the relative performance and the critical diameter of IEE based on 1 — AN monosolution; 2 — binary solutions of ammonium and sodium nitrate; 3 — ammonium nitrate and calcium

Parameters	IEE porosity 0,20			IEE porosity 0,25		
	1	2	3	1	2	3
Critical diameter (d_{cr}), mm	51,7	52,1	15,6	38,1	38,5	12,0
Relative performance (f)	0,769	0,736	0,759	0,751	0,731	0,739

The relative performance of systems shown in the table has been estimated respectively to the standardized TNT-containing packaged explosive Ammonite No.6-ZhV.

As the table shows, for the packaged emulsion explosives with d_{crit} below 32 mm in quality of the dispersed phase it should be used a binary oxidizing solution containing mixture of ammonium nitrate and calcium nitrate, in an optimal ratio corresponding to salts crystallization minimum temperature.

These data are confirmed with the results of research presented in [10], according to which the ammonium nitrate replacement with calcium nitrate resulted in a slight IEE efficiency decrease (about 2 %). A similar substitution with sodium nitrate leads to efficiency decrease of 7,5 %.

As a result of complex research designed are the packaged IEE of "UKRAINIT-P" mark (Patent UA 63689). Under the conditions of the "Promvzryv", CJSC (Zaporizhia, Ukraine) landfill we manufactured and tested UKRAINIT-P cartridges with emulsion water content of 6...9 wt.%. The experimental detonation velocity measurements show that with decreasing water content of 1 % by weight, the UKRAINIT-P cartridges' detonation velocity is increased by 100...150 m/s reaching Ammonite No.6-ZhV ($D=4900$ m/s) characteristics. Reducing the water content below 6 % by weight is not practical because in such case the IEE obtaining process requires technological temperatures above 105 °C.

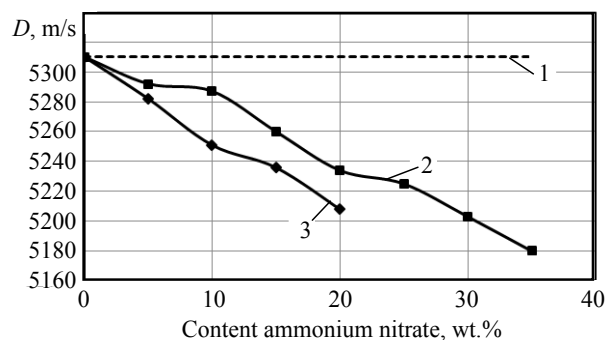


Fig. 3. Changes in IEE detonation velocity with respect to the degree of ammonium nitrate replacement with calcium nitrate (2) and sodium nitrate (3) compared to the IEE on the basis of ammonium nitrate monosolution (1)

Conclusions. This article exposes the ammonium nitrate-based oxidizer's determining influence on technological and detonation parameters of emulsion explosives. We established that the sodium nitrate use as an oxidant in the composition of packaged systems is limited by its solubility characteristics and decreased IEE detonation. It has been found that for obtaining packaged IEE of diameter 32 mm or less it is advisable to use as an oxidant the aqueous solution of ammonium and calcium nitrates' mixture of following composition, wt. %: H_2O 7,0...10,0; $\text{Ca}(\text{NO}_3)_2$ 27,5...31,5; NH_4NO_3 58,5...65,5. It has been observed and confirmed that a decrease in the water content of 1,0 % by weight concurs to the detonation velocity increasing by 100...150 m/s.

Література

1. Wang, X. *Emulsion explosives* / X. Wang. – Beijing: Metallurgical Industry Press, 1994. — 388 p.
2. Колганов, Е.В. Эмульсионные промышленные взрывчатые вещества / Е.В. Колганов, В.А. Соснин. — Дзержинск: ГосНИИ “Кристалл”, 2009. — . — Кн. 1: Составы и свойства. — 2009. — 592 с.
3. Розробка і впровадження емульсійних вибухових речовин на кар'єрах України: монографія / В.П. Купрін, І.Л. Коваленко, М.І. Іщенко, В.Ф. Монаков, О.І. Макаров; ред.: В.П. Купрін; ДВНЗ “Укр. держ. хіміко-технол. ун-т”. — Д., 2012. — 244 с.
4. Физика взрыва: [в 2 т.] / С.Г. Андреев [и др.]; под ред. Л.П. Орленко. — 3-е изд., испр. — М.: Физматлит, 2004. — . — Т. 1. — 2004. — 823 с.
5. Маторин, А.С. Водосодержащие взрывчатые вещества местного приготовления: монография / А.С. Маторин, В.М. Павлютенков; [отв. ред. А.В. Гальянов]; РАН, УрО, Ин-т горного дела. — Екатеринбург: УрО РАН, 2004. — 192 с.
6. Рябухин, А.Г. Энергия Гиббса гидратации катионов (s^2p^6) / А.Г. Рябухин // Известия Челябинского научного центра УрО РАН. — 2000. — Вып. 4. — С. 79 — 80.
7. Горинов, С.А. Оценка детонационной способности эмульсионных взрывчатых веществ / С.А. Горинов, В.П. Куприн, И.Л. Коваленко // В кн.: Высокоэнергетическая обработка материалов. — Днепропетровск: Арт-пресс, 2009. — С. 18 — 26.
8. Теоретическая оценка влияния химической природы окислителя на детонационные характеристики эмульсионных взрывчатых веществ / С.А. Горинов, В.П. Куприн, И.Л. Коваленко, Е.П. Собина // Развитие ресурсосберегающих технологий во взрывном деле: доклады всероссийской науч. конф. — Екатеринбург: ИГД УрО РАН. — 2009. — С. 191 — 201.
9. Горинов, С.А. Выбор химического состава окислительной фазы эмульсионных взрывчатых веществ для отбойки крепких горных пород скважинами уменьшенного диаметра / С.А. Горинов, В.П. Куприн, Н.В. Савченко // Вісн. КрНУ ім. М. Остроградського. — 2012. — Вип. 5(76). — С. 56 — 60.
10. Кукиб, Б.Н. О влиянии химического состава окислительной фазы эмульсии на скорость детонации и относительную работоспособность эмульсионных взрывчатых веществ / Б.Н. Кукиб // Взрывное дело. — 2013. — Вып. 110/67. — С. 111 — 123.

References

1. Wang, X. (1994). *Emulsion Explosives*. Beijing: Metallurgical Industry Press.
2. Kolganov, E.V. and Sosnin, V.A. (2009). *Industrial Emulsion Explosives. Vol. 1, Composition and Properties*. Dzerzhinsk: JSC “GosNII “Kristall”.
3. Kuprin, V.P., Kovalenko, I.L., Ischenko, M.I. and Monakov, V.F. (2012). *Development and Application of Emulsion Explosives in Ukrainian Quarries*. Dnepropetrovsk: Ukrainian State University of Chemical Technology.
4. Orlenko, L.P. (2004). *Physics of Explosions. Vol. 1*. 3rd ed. Moscow: Fizmatlit.
5. Matorin, A.S. and Pavlyutenkov, V.M. (2004). *Water-containing Explosives of Local Preparation*. Ekaterinburg: Ural Branch of the Russian Academy of Sciences.
6. Ryabuchin, A.G. (2000). Gibbs Energy of a Cations (s^2p^6) Hydration. *Proceedings of the Chelyabinsk Scientific Center*, 4, 79-80.

7. Gorinov, S.A., Kuprin, V.P. and Kovalenko, I.L. (2009). Evaluation of the Detonation Ability Emulsion Explosives. In V.V. Sobolev (Ed.), *High Energy Materials Processing* (pp. 18-26). Dnepropetrovsk: Art-press.
8. Gorinov, S.A., Kuprin, V.P., Kovalenko, I.L. and Sobina, E. P. (2009). Theoretical Evaluation of the Influence of the Chemical Composite of the Oxidant on the Detonation Characteristics of Emulsion Explosives. In V.G. Shemenev (Ed.), *Proceedings of the International Conference on Development of Resource Saving Technologies in the Blasting (3rd Ural Mining Industry Forum)* (pp. 191-201). Yekaterinburg, Russia: Institute of Mining of Ural Branch of RAS.
9. Gorinov, S., Kuprin, V. and Savchenko, N. (2012). Chemical Composition of Oxidizing Phase of Emulsion Explosives for Solid Rocks Breaking With Reduced Diameter Holes. *Transactions of Kremenchuk Mykhailo Ostrohradskyi National University*, 5 (76), 56-60.
10. Kukib, B.N. (2013). Influence of the Chemical Composition Oxidizes Solution on Detonation Velocity and Performance of Emulsion Explosives. *Vzryvnoye Delo*, 110(67), 111-123.

АНОТАЦІЯ / АННОТАЦИЯ / ABSTRACT

І.Л. Коваленко, В.П. Купрін. Патроновані енергоконденсовані системи. Вибір компонентів окисника. Розглянутий вплив складу окисника на основі аміачної селітри на технологічні та детонаційні параметри емульсійних енергоконденсованих систем для гірничої промисловості. Показано, що використання у складі окисника натрій нітрату обмежено його розчинністю і зниженням детонаційних характеристик енергоконденсованих систем. Встановлено, що для одержання високоефективних патронованих систем як окисник необхідно використовувати водний розчин нітратів амонію та кальцію при вмісті води 7,0...10,0 % мас. Показано, що зі зменшенням вмісту в системі води на 1,0 % мас. швидкість детонації енергоконденсованих систем зростає на 100...150 м/с.

Ключові слова: енергоконденсована система, окисник, аміачна селітра, кальцій нітрат, вміст води.

И.Л. Коваленко, В.П. Куприн. Патронированные энергоконденсированные системы. Выбор компонентов окислителя. Рассмотрено влияние состава окислителя на основе аммиачной селитры на технологические и детонационные параметры эмульсионных энергоконденсированных систем для горной промышленности. Показано, что использование в составе окислителя натрий нитрата ограничено его растворимостью и снижением детонационных характеристик энергоконденсированных систем. Установлено, что для получения высокоэффективных патронированных систем в качестве окислителя необходимо использовать водный раствор нитратов аммония и кальция при содержании воды 7,0...10,0 % масс. Показано, что с уменьшением содержания в системе воды на 1,0 % масс. скорость детонации энергоконденсированных систем возрастает на 100...150 м/с.

Ключевые слова: энергоконденсированная система, окислитель, аммиачная селитра, кальций нитрат, содержание воды.

I.L. Kovalenko, V.P. Kuprin. Energy condensed packaged systems. Oxidizer components selection. The influence of the ammonium nitrate-based oxidizer composition on the technological and detonation parameters of the emulsion energy condensed systems for mining industry has been considered. It is shown that the use of sodium nitrate as a part of oxidizer is limited by its solubility and decreasing of detonation characteristics of energy condensed systems. It is found that for obtaining of highly efficient packaged systems an aqueous solution of ammonium or calcium nitrate with water content 7...10 % by weight should be used as oxidizer. It is shown that with decreasing of water content in the system by 1.0 % by weight the detonation velocity of energy condensed systems increases by 100...150 m/s.

Keywords: energy condensed system, oxidizer, ammonium nitrate, calcium nitrate, water content.

Reviewer Dr. techn. sciences, Prof. Odesa nat. polytechnic univ. Erayzer L.M.

Received August 27, 2014.