ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

UDC 661.52:662.2

I.L. Kovalenko, PhD, Assoc.Prof.,
V.P. Kuprin, Doctor of Chemistry, Professor,
Ukrainian State University of Chemical Engineering, Dnipropetrovsk,
D.V. Kiyaschenko,
"Ukrvybukhtekhnologia", LLC

ENERGY CONDENSED PACKAGED SYSTEMS. COMPOSITION, PRODUCTION, PROPERTIES

Introduction. Mining enterprises of Ukraine annually consume up to 150 thousand tons of industrial explosives. Until recently industrial explosives were composed of TNT — highly toxic substance that is prohibited in Europe since 1993. Transition of the mining industry on the use of domestic high-performance, safe emulsion explosives (EE) [1] almost completely renounce the use of TNT on open cast mining. At the same time in underground conditions the use of EE is limited due to a number of requirements for such systems.

Literature review. It is known [1] that EE are the inverse emulsions of highly concentrated solution of oxidizer (91...93 wt %) in the hydrocarbon medium (7,0...9,0 wt %) sensitized by pore-forming components (gas generating additives). Widespread use of EE in underground mining assumes their production in package form with preservation of stability and high detonation parameters. In [2] it is shown that the best option of oxidant conforming to the specified requirements, has the following composition, wt %: H_2O 7,0…10,0; $Ca(NO_3)_2$ 27,5…31,5; NH_4NO_3 58,5…65,59. The composition of specified oxidant has a lower crystallization temperature compared to the monosolution of ammonium nitrate and binary solution "ammonium nitrate — sodium nitrate". This provides a maximum thermal effect of reaction of explosive conversion when interacting with a hydrocarbon medium.

Usually [3] oil and products of its processing (oil, diesel fuel, industrial oils, waxes, etc.) are used as fuel phase in energy condensed emulsion systems. At the same time the value of the specific heat of fuel combustion is considered as the main parameter. This value is determined by the relation of carbon and hydrogen content in the molecule (H/C) and has maximum value for paraffinic hydrocarbons and minimum value for aromatic ones. Besides, the viscosity characteristics of fuel phase are very important for obtaining the emulsion with specified technological parameters.

Energy condensed emulsion systems which are used as industrial explosives have mixtures mechanism of detonation, so the chemical reaction proceeds between the oxidant and reductant that are not in molecular contact. According to [4], the high detonation ability of ammonium nitrate explosives can be provided by increasing the contact area of oxidizer and fuel and by the temperature increasing in chemical reaction zone. The width of chemical reaction zone determines the critical detonation diameter [5]. In its turn, the width of chemical reaction zone is determined by the speed of heat release. The speed of heat release depends on the size of oxidant globules in the emulsion, the oxidation rate of fuel phase and the pore size of emulsion, the carrier of which is sensitizer.

For the production of energy condensed packaged emulsion systems it is necessary to solve the problem of producing highly viscous emulsion with minimal size of particles of the dispersed phase. Such an emulsion after entering the special materials — sensitizers — provides high detonation parameters and sensitivity to detonator cap.

The problem of obtaining the highly dispersed highly viscous emulsions can be solved by static mixers of nozzle type. In the nozzle the oxidant solution is crushed to the smallest drops in the form of

DOI 10.15276/opu.1.45.2015.27

torch and mixed with the fuel phase. The resulting mixture is pressed through the outlet of the mixer so the required viscosity emulsion is obtained. The disadvantages of known devices are the need to change the nozzles to achieve the required degree of dispersion and the inability to adjust the viscosity of resulting emulsion without changing the size of the outlet for the emulsion. Moreover, it is believed [3] that the static mixers are preferably used for pre-emulsification, followed by treatment of emulsion in the dynamic mixer of rotor-stator type.

Aim of the Research is to carry out the scientific foundation of the choice of fuel phase and technology of emulsion production based on binary aqueous solution of ammonium and calcium nitrates, providing production of energy condensed packaged systems with required properties.

Main Body. The influence of nature of the fuel phase on the character of thermal decomposition systems “ammonium nitrate — fuel component” was investigated by differential thermal analysis (setting TERMOSKAN-2, scientific-production enterprise “Analitpribor”, St. Petersburg) at a scan rate of 20 deg/min, sample weight 50 mg. The character of thermolysis of studied systems can be estimated by the temperature of the beginning of intensive exothermic decomposition (t_b) and the speed of progress of differential temperature (v_t), the characteristic temperature of exothermic peak (t_{peak}) and its intensity (h_{peak}). The intensity of exothermic peak h_{peak} is defined as the difference between differential temperatures of the top of peak and the base line temperature t_b. By area of the exothermic peak on the thermograms the thermal effects and the relative coefficient of system heat release K are determined. K is calculated as the ratio of the exothermic peak area to the ammonium nitrate peak area. The results of thermal studies are given in Table 1.

Table 1

The character of thermal decomposition of stoichiometric mixtures “ammonium nitrate — fuel component”

System	t_b, °C	v_t, deg/min	t_{peak}	h_{peak}	K
Ammonium nitrate (AN)	230	1,47	276	2,13	1
AN — diesel fuel	223	2,8	282	3,05	2,44
AN — industrial oil I-20	250	7,9	290	13,09	3,67
AN — fuel oil	216	8,95	262	11,79	9,04
AN — paraffin	250	6,6	282	4,19	1,91
AN — ceresin	253	4,2	283	5,66	2,23
AN — paraffin petroleum wax	255	5,86	290	5,62	2,22
AN — sunflower oil	230	16,7	255	17,7	10,91
AN — linseed oil	216	21,3	248	20,6	11,89

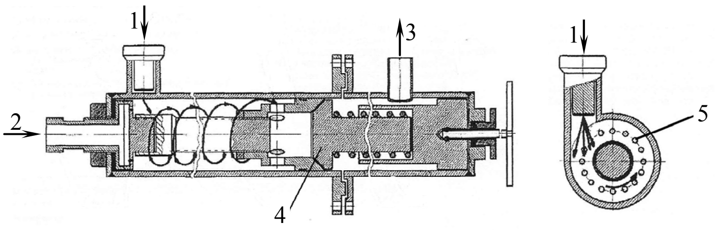
Unexpectedly weak influence of diesel fuel (Table 1), even in comparison with the difficult oxidizable saturated hydrocarbon, can be explained by two factors: the significant fuel evaporation during the sample heating and the presence of antioxidant additives in the product. The effectiveness of the fuel oil is probably caused by the presence of sulfur in its composition, which is a catalyst for the decomposition of ammonium nitrate (GOST 2-85, DSTU 7370: 2013) as well as products of incomplete oxidation (resins) containing metals of variable valence (V, Ni, Fe).

Considering that the unsaturated hydrocarbons are oxidized much more easily then limit, cyclic and aromatic compounds, vegetable oils have a much greater impact on the thermolysis of ammonium nitrate (table 1). Thus, the relative coefficient of heat release K of systems containing sunflower and linseed oil 3...5 times greater than heat release of systems with industrial oils and waxes, and the speed of progress of differential temperature is 2...3,5 times greater. With increasing the degree of unsaturation of fatty acids included in the composition of oils their oxidation speed increases.

Thus, fuel phase of energy condensed emulsion systems must be based on esters of polyunsaturated acids (vegetable oils) or combinations thereof with mineral oil. Ceresin or oil wax can be used as structuring additive.

To produce the energy condensed emulsion systems it was developed an emulsion production apparatus which overcomes the main drawbacks of the known static mixers [6] (Fig. 1).

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)



a *b*

Fig. 1. Emulsion production apparatus: longitudinal section (a): 1 — supply of oxidizer solution, 2— supply of fuel phase, 3— outlet of the resulting emulsion, 4— valve mechanism; cross-section along the axis of input of oxidizer solution(b): 5 — distribution device for the fuel phase

Apparatus has some differences. Insertion of oxidizer solution takes place by nozzles which is tangentially mounted in the wall of body. Inlet pipe for the fuel phase has a distribution device with holes. The outlet for the emulsion is placed into the wall of body of the valve mechanism provided with a regulating screw. The degree of dispersion of the emulsion in the apparatus is determined by flow rate of the oxidant solution (6...35 m/s), viscosity of the resulting emulsion is regulated by the valve mechanism.

Table 2 shows the values of viscosity and dispersion of emulsions prepared using this apparatus. The size of particles of emulsion dispersed phase was evaluated by light microscopy (microscope Carl Zeiss NU2, digital eyepiece SIGETA UCMOS 05100KRA 5,1MPx). The viscosity of emulsion was determined by viscometer Brookfield DV-E with a range of discrete velocities of working spindle rotation.

Table 2

Characteristics of the emulsion obtained in the emulsifying apparatus

№	The speed of oxidizer solution supply, m/s	The load on the valve, kg	Viscosity at t=26 °C, Pa·s	Dispersity of the emulsion, mcm
1	6,4	0	49,2	5,3
2	23,1	0	87,8	2,7
3	26,4	0	98,2	2,3
4	26,4	33,0	115,6	2,2
5	28,4	33,0	118,4	2,0
6	28,5	50,0	$> 10^3$	1,3

To assess the feasibility of the two-step emulsification the resulting emulsion in the static mixer was further dispersed using the colloid mill IKA MK 2000 and dispersant IKA Ultra-TURRAX UTL (the number of rotor revolutions in both cases was 7848 min^{-1}).

According to test results it is found that two-steps emulsification using mentioned devices increases dispersion of the emulsion no more than on 5...10 % in comparison with the one-step process. In this case in emulsion prepared using a colloid mill MK the crystal nuclei are detected on the second day. The results of X-ray diffraction identify them as ammonium nitrate.

Effect of intensive exposure on energy condensing system with two-steps emulsification is proved by tests of packaged emulsion explosives manufactured on the basis of obtained emulsion.

Table 3 shows the values of the detonation velocity for EE with different water content in the emulsion. Detonation velocity was determined experimentally at the landfill of “Promvzryv”, PJSC (Zaporizhia, Ukraine) by recorder MicroTrap VOD DATA.

Tests have shown (Table 3) that use of two-steps emulsification scheme with dispersant Ultra-TURRAX UTL increases detonation velocity of energy condensing system not more than 4 %. The use of colloid mill reduces detonation characteristics and sensitivity of EE. Intense impact to the emulsion in a colloid mill leads to destabilization of the system, the probability of which increases with increasing of salt concentration in the dispersed phase.

The experience of making and using the energy condensed packaged systems at low temperatures shows the need for the insertion of plasticizing additives to the system. Liquid chlorinated paraffin CP-470 containing 45...49 wt% of combined chlorine was used as such a additive. The choice of chlorinated paraffin as a plasticizer caused by its rheological properties and the specific impact on energy condensed systems. According to the literature [7] in small amounts (up to 1 wt%) chlorinated paraffins cause a sensitizing effect on the emulsion system, i.e. increase their sensitivity to detonation impulse.

Table 3

The detonation velocity of the emulsion explosive cartridges 32 mm in diameter (open charge) at different methods of emulsification and water content in emulsion.

Emulsification technology		detonation velocity of EE, m/s at water content in emulsion:	
		9 wt %	7 wt %.
One-step emulsification (static mixer)		4643	4828
Two-steps emulsification	static mixer + Ultra-TURRAX UTL	4812	4850
	static mixer + MK 2000	4624	3868

Indeed, the insertion of 1 wt% of CP-470 provides an earlier expansion of the emulsion (Fig. 2).

Such an influence of the additives can be explained by the thermal behavior of the chlorinated paraffin. According to [8] at temperatures of more than 150...200 °C chlorinated paraffins cleave off the hydrogen chloride, which has a catalytic effect on the thermolysis of ammonium nitrate [9, 10]. The increase of CP-470 of more than 1 wt% gives no further effect and a significant amount of chlorinated paraffin (more than 10 wt%) acts on the system as a flame retardant

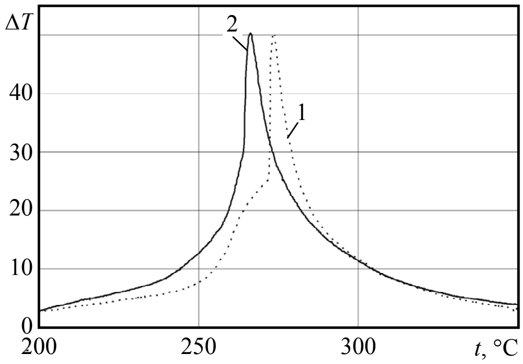


Fig. 2. Thermogram of decomposition of energy condensed emulsion systems: without plasticizer (1); with content of 1 wt% of CP-470 (2)

Results. According to the results of studies of the effect of the fuel phase on the rheological parameters of emulsions and the nature of their thermal decomposition the compounds of the fuel phase (the dispersion medium) of energy condensed packaged emulsion systems have been developed. The fuel component is a solution of the composition of dimeric surfactants based on vegetable fats in a mixture of industrial oil and products of processing of plant raw materials. The formulations of fuel component of packaged emulsions expanded the existing assortment of product "Emulsifier "Ukrainit" and were made to the existing specifications (TU U 20.5-19436711-002:2012).

The use of proposed static mixer for emulsifying of energy condensed systems allowed to obtain an emulsion with dispersion of 1,3...1,8 mcm and viscosity greater than 10^3 Pa·s (t=26 °C) at a flow rate of oxidant solution over 28,5 m/s and the load on the valve 50 kg. On the basis of received energy condensed systems a number of packaged emulsion explosives mark Ukrainit-P [11] is developed for use in mines not dangerous on gas and dust (Table 4).

Landfill and industrial tests in mines not dangerous on gas and dust have shown that packaged emulsion explosives Ukrainit-P at brisance do not concede the staffing TNT explosives — Ammonite No.6-ZhV. They can be used as main charge of middleware detonator (marks "P-S" and "P-SA") for initiation of charges of emulsion and mixture explosive in boreholes of any diameter. Mark "P-P" can be used as main charge.

Production of energy condensed packaged systems of mark Ukrainit-P is implemented in terms of the base storage of "Promvzryv", PJSC (Zaporizhia, Ukraine). The production cycle includes the step of preparing the solution of oxidizing agent, one-step emulsification in the static mixer, sensitization of the emulsion system and insertion of plasticizers, patronage of the finished emulsion explosives in a polymer shell, cooling of patrons, labeling and bagging.

For sensitization of low sensitive emulsion it is used the glass microspheres of firm 3M mark K1 with true density 0,12…0,14 g/cm^3 with average diameter of particles about 100 micron. Microspheres are inserted in hot emulsion (t=90…95 °C) with mixer of original construction, which provides uniformity of distribution and integrity of the microspheres. On the step of insertion of microspheres chlorinated paraffin CP-470 is inserted into the emulsion as a plasticizer. Later the resulting explosive

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

Ukraine-P is supplied with screw pump in ChubMaker 2500 S/N 16558 for the production of patrons in diameter from 32 to 90 mm.

Table 4

Characteristics of packaged emulsion explosives of mark Ukrainit

Indicators	Marks of EE Ukrainit-P		
	P-S	P-SA	P-P
Density at 30±10 ^{0}C, g/cm^3	1,00… 1,30		
Oxygen balance, %	–0,3…–0,5	–0,5…–0,15	–0,3…–1,5
Heat of explosion, kJ/kg (estimated)	3400…3500	3700…3900	3150…3200
Specific volume of gas explosion, dm^3/kg	840…860	820…830	840…860
Detonation velocity of the charge, m/s (at least)	4900	4800	4400
Critical diameter of the open charge, mm	20…24	20…23	35…40
Toxic gases of explosion (scaling to CO), l/kg	Up to 15,0	Up to 25,0	Up to 20,0

Conclusions. It is studied the nature of the thermal decomposition of the energy condensed systems based on ammonium nitrate according to the nature of the fuel component. The influence of emulsification technology of the energy condensed systems on physical, chemical and detonation characteristics of emulsion explosives is considered. The possibility of obtaining the energy condensed emulsion systems with dispersion of 1,3...1,8 mcm and viscosity greater than 10^3 Pa·s with one-step emulsification in the static unit of original design is shown. Composition and technology of production of the energy condensed packaged emulsion systems of mark Ukrainit-P are developed.

Література

1. Купрін, В.П. 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.
2. Kovalenko, I.L. Energy condensed packaged systems. Oxidizer components selection / I.L. Kovalenko, V.P. Kuprin // Пр. Одес. політехн. ун-ту. — 2014.— Вип. 2(44).— С. 191 — 195.
3. 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.
4. Концепция разработки рецептуры и технологии изготовления ЭМВВ с высокой детонационной способностью / О.Ф. Мардасов, В.П. Глинский, Н.К. Шалыгин [и др.] // Взрывное дело. —2008. — № 99/56. — С. 162 — 170.
5. 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.
6. Пат. 69553 Україна, МПК B01F 3/08, C06B 21/00, C06B 47/00. Апарат отримання емульсії для емульсійної вибухової речовини / Купрін В.П., Савченко М.В., Кіященко Д.В., Сергієнко І.Д., Дзюбєнко С.А., Рахімов Р.Х.; заявник та патентовласник ТОВ “Укрвибухтехнологія”. — № u201202373; заявл. 28.02.2012; надр. 25.04.2012, Бюл. № 8.
7. Wang, X. Emulsion explosives / X. Wang. — Beijing: Metallurgical Industry Press, 1994. — 388 p.
8. Muir, D.C.G. Chlorinated Paraffins / D.C.G. Muir, G.A. Stern, G. Tomy // The Handbook of Environmental Chemistry / ed. by J. Paasivirta. — Berlin, Heidelberg: Springer-Verlag, 2000. — Vol. 3. — PP. 203 — 236.
9. Chaturvedi, S. Review on thermal decomposition of ammonium nitrate / S. Chaturvedi, P.N. Dave // Journal of Energetic Materials. — 2013. — Vol. 31, Issue 1. — PP. 1 — 26.
10. Коваленко, И.Л. Влияние хлоридов феррума (III) и купрума (II) на термическое разложение энергонасыщенных систем на основе аммиачной селитры / И.Л. Коваленко // Пр. Одес. політехн. ун-ту. — 2013.— Вип. 3(42). — С. 233 — 237.

11. Пат. 63689 Україна, МПК C06B 27/00, C06B 31/02. Патронована емульсійна вибухова речовина "Україніт-П" / Купрін В.П., Купрін О.В., Риков С.В., Савченко М.В.; заявник та патентовласник ТОВ "Укрвибухтехнологія". — № u201110308; заявл. 23.08.2011; надр. 10.10.2011, Бюл. № 19.

References

1. 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.
2. Kovalenko, I.L. and Kuprin, V.P. (2014). Energy condensed packaged systems. Oxidizer components selection. *Odes'kyi Politechnichnyi Universytet. Pratsi*, 2, 191-195.
3. Kolganov, E.V. and Sosnin, V.A. (2009). *Industrial Emulsion Explosives. Vol. 1, Composition and Properties.* Dzerzhinsk: JSC "GosNII "Kristall".
4. Mardasov, O.F., Glinski, V.P., Shalygin, N.K., Babintseva, V.V. and Isakova, L.V. (2008). The concept of formulation development and manufacturing technique of emulsion explosives with high detonation ability. *Vzryvnoye Delo*, 99(56), 162-170.
5. Orlenko, L.P. (2004). *Physics of Explosions. Vol. 1.* 3rd ed. Moscow: Fizmatlit.
6. Ukrvybukhtekhnologia, LLC (2012). *Apparatus for producing emulsion for emulsion explosive substance*. Ukraine Patent: UA 69553.
7. Wang, X. (1994). *Emulsion Explosives*. Beijing: Metallurgical Industry Press.
8. Muir, D.C.G., Stern, G.A. and Tomy, G. (2000). Chlorinated Paraffins. In J. Paasivirta (Ed.), *The Handbook of Environmental Chemistry* (Vol. 3, pp. 203—236). Berlin, Heidelberg: Springer-Verlag.
9. Chaturvedi, S. and Dave, P.N. (2013). Review on thermal decomposition of ammonium nitrate. *Journal of Energetic Materials*, 31(1), 1-26.
10. Kovalenko, I.L. (2013). The influence of ferrum (III) and cuprum (II) chlorides on thermal decomposition of ammonium nitrate based energy systems. *Odes'kyi Politechnichnyi Universytet. Pratsi*, 3, 233-237.
11. Ukrvybukhtekhnologia, LLC (2011). *"Ukrainit-P" packaged emulsion explosive*. Ukraine Patent: UA 63689.

АНОТАЦІЯ / АННОТАЦИЯ / ABSTRACT

І.Л. Коваленко, В.П. Купрін, Д.В. Кіященко **Патроновані енергоконденсовані системи. Склад, отримання, властивості.** Наведено обгрунтування вибору складу паливної фази та оптимальної технології одержання емульсії на основі бінарного розчину нітратів амонію та кальцію, що забезпечують одержання патронованих енергоконденсованих систем з заданими властивостями. Досліджено термічне розкладання енергоконденсованих систем на основі аміачної селітри. Показано, що паливна фаза емульсійних систем повинна базуватись на ефірах поліненасичених кислот або їх комбінації з нафтопродуктами, а структуруючою добавкою може бути використано церезин або нафтовий віск. Розглянуто вплив технології отримання енергоконденсованих систем на фізико-хімічні та детонаційні характеристики емульсійних вибухових речовин. Показано можливість одержання емульсійних систем з дисперсністю 1,3…1,8 мкм та в'язкістю понад 10^3 Па·с в апараті оригінальної конструкції. Показано сенсибілізуючу дію хлорпарафіну ХП-470 на термоліз емульсійної енергоконденсованої системи. Розроблено склад і технології отримання патронованих емульсійних енергоконденсованих систем марки Україніт-П для підземних гірничих розробок в шахтах, безпечних за газом і пилом.

Ключові слова: енергоконденсована система, горючий компонент, технологія, змішувач.

И.Л. Коваленко, В.П. Куприн, Д.В. Киященко. **Патронированные энергоконденсированные системы. Состав, получение, свойства.** Приведено обоснование выбора состава топливной фазы и оптимальной технологии получения эмульсии на основе бинарного раствора нитратов аммония и кальция, обеспечивающих получение патронированных энергоконденсированных систем с заданными свойствами. Исследовано термическое разложение энергоконденсированных систем на основе аммиачной селитры. Показано, что топливная фаза эмульсионных систем должна базироваться на эфирах полиненасыщенных кислот или их комбинации с нефтепродуктами, а как структурирующая добавка могут быть использованы церезин или нефтяной воск. Рассмотрено влияние технологии получения энергоконденсированных систем на физико-химические и детонационные характеристики эмульсионных взрывчатых веществ. Показана возможность получения эмульсионных систем с дисперсностью 1,3…1,8 мкм и вязкостью более 10^3 Па·с в аппарате оригинальной конструкции. Показано сенсибилизирующее действие хлорпарафина ХП-470 на термолиз эмульсионной энергоконденсированной системы. Разработаны состав и технология получения патронированных эмульсионных энергоконденсированных систем марки Украинит-П для подземных горных разработок в шахтах, не опасных по газу и пыли.

Ключевые слова: энергоконденсированная система, горючий компонент, технология, смеситель.

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

I.L. Kovalenko, V.P. Kuprin, D.V. Kiyaschenko. **Energy condensed packaged systems. Composition, production, properties.** In this paper it is presented the substantiation of choice of fuel phase composition and optimal technology of emulsion production on the basis of binary solution of ammonium and calcium nitrates, which provide the obtaining of energy condensed packaged systems with specified properties. The thermal decomposition of energy condensed systems on the basis of ammonium nitrate is investigated. It is shown that the fuel phase of emulsion systems should be based on esters of polyunsaturated acids or on combinations thereof with petroleum products. And ceresin or petroleum wax can be used as the structuring additive. The influence of the technology of energy condensed systems production on the physicochemical and detonation parameters of emulsion explosives is considered. It is shown the possibility of obtaining of emulsion systems with dispersion of 1.3...1.8 microns and viscosity higher than 10^3 Pa·s in the apparatus of original design. The sensitizing effect of chlorinated paraffin CP-470 on the thermolysis of energy condensed emulsion system is shown. The composition and production technology of energy condensed packaged emulsion systems of mark Ukrainit-P for underground mining in mines not dangerous on gas and dust are developed.
Keywords: energy condensed system, combustible component, technology, mixer.

Received January 29, 2015