Cartridged and granulated explosive substances of grade Ukrainit for underground mines

Ihor Kovalenko

Ph.D., Assoc. Professor
Ukrainian State Unversity of Chemical Technology,
Dnipro, Ukraine
E-mail: il-kovalenko@mail.com

Nikolay Stupnik

D.Sc., Prof.,
Kryvyi Rih National University,
Kryvyi Rih, Ukraine
E-mail: knu@alba.dp.ua

Mikhail Korolenko

PrJSC "Zaporiz'kyi Zalizorudnyi Kombinat",
Zaporozhie, Ukraine
E-mail: info@zgrk.com.ua

Dmitriy Kiyaschenko

Co.Ltd "Ukrvzryvtehnologiya",
Kharkov, Ukraine
E-mail: kiyashenko@yandex.ua

Alexandr Batareev

PJSC "EVRAZ Sukha Balka",
Kryvyi Rih, Ukraine
E-mail: vopros@evraz.com

Abstract
The paper presents a part of set of operations on change of underground mines for trotyl-free explosive substances (ES). The purpose is development and introduction granulated and cartridged trotyl-free explosive substances with high detonation and technological parameters in the underground mines of Ukraine. The unique structure of fuel phase and unparalleled technology of obtaining of highly-stable granulated ES Ukrainit-ANFO on the basis of agrarian ammonium nitrate is created. Ukrainit-ANFO is intended for pneumocharging of holes and wells of small diameter, possess high level working capacity and safety, minimum toxicity of explosion products, long guarantee period (3 months). Scientifically based approach to creation of formulas and technology of obtaining cartridged emulsion ES Ukrainit-P is implemented. According to functional purpose, cartridges Ukrainit-P are universal and intended for formation blast-hole charges, for initiation (as intermediate detonator) of charges of emulsion and granulated ES in wells and holes of any diameter, and also for crushing of oversize material. High parameters of working capacity and small critical diameter allow production of cartridges of any diameter (from 32 mm). The range and technology of developed of granulated and cartridged ES of grade Ukrainit in combination with filling emulsion ES Ukrainit provide complex solution of problem of underground mines Ukraine change for trotyl-free ES.
Key words: GRANULATED EXPLOSIVE SUBSTANCES, AMMONIUM NITRATE, MODIFICATION, EMULSION, CARTRIDGED EMULSION EXPLOSIVE SUBSTANCES

Relevance

One of tasks of complex conversion of underground mines of Ukraine to the safe trotyl-free explosive substances (ES) is refusal of application of standard trotyl-containing materials, namely, the granulated Grammonite 79/21 and cartridged Ammonite No 6ZhV. Trotyl is highly toxic substance which causes more than 30 occupational diseases of staff and is dangerous in use and generates a large amount of harmful gases in case of explosion. Safe alternative to cartridges Ammonite No 6ZhV and Grammonite 79/21 are cartridged emulsion ES and granulated ES for pneumocharging.

In underground conditions, cartridged ES are used: 1) for blast-hole charges formation; 2) for crushing of oversize material of rocks in the form of pressure charges; 3) intermediate detonator of borehole charges. These application areas cause distinction of requirements to detonation parameters of cartridged emulsion ES that complicates introduction of similar ES in underground mines of Ukraine.

Application of mixed trotyl-free explosive substances on the basis of the granulated ammonium nitrate in underground mines is economically sound. Experience of the USA and Canada shows that use of such ES on the basis of system "ammonium nitrate / liquid combustible component" (AS-DT, Igdanit, ANFO, granulites) allows reduction of the cost of explosive operation by 40 – 50% of [1]. However, the majority of the granulated ES for pneumocharging are characterized by small physical stability in time, separation when pneumotransporting, insufficient detonation parameters, namely, low speed of detonation and big critical diameter. It does not allow such ES to be used effectively for pneumatic charging of holes and wells of small diameter (32 – 80 mm). Moreover, majority of known trotyl-free granulated systems [2] contain oil products as liquid fuels which form toxic aerosols in case of pneumocharging.

Purpose and research problems

The paper objective is development and introduction to the underground mines of Ukraine of granulated and cartridged trotyl-free explosive substances with high detonation and technological parameters. Implementation of objective means solution of the following tasks:

- development of composition of fuel phase and technology of obtaining of highly effective granulated ES with guaranty period of storage at least 1 month;

- development of structures and technology of cartridged emulsion ES used for forming of blast-hole charges, pressure charges for crushing of oversize material and as intermediate detonators.

Technology of highly stable granulated ES for pneumocharging of Ukrainit of ANFO.

Based on the generalized experience of application of various granulated ES in mines, which are not dangerous on gas and dust, the main requirements to ANFO can be formulated: 1) physical stability within at least 30 days; 2) maintenance of balance oxidizer-fuel in each part of charge (perfectly – in each granule); 3) strength of granules, the nitrate should maintain pneumatic transportation and charging; 4) absence of oil products in composition; 5) detonation parameters should provide effective application in holes and wells of small diameter (32 – 80 mm).

The detonation mechanism, at which chemical reaction of explosive transformation takes place between oxidizer and reducer, which are not in molecular contact [3], is inherent in mixed power condensed systems on the basis of mixed ammonium nitrate. In this case, increase in temperature in a zone of chemical reaction, which width determines the critical diameter of detonation [3] can provide high detonation ability. In turn, width of chemical reaction zone is determined by the thermal emission speed, which directly depends on the speed of oxidation of combustible phase and nature of sensitizer.

For development of composition of liquid fuel phase of granulated ES, it has been systematically investigated influences of nature of combustible component on the nature of thermo-decompounding and time of induction of autogenous ignition [2] of systems “ammonium nitrate / liquid combustible component” of sensitizing agent.

Nature of thermo-decompounding was evaluated by efficiency of oxidation of fuel ammonium nitrate (Ammonium nitrate) and products of its desintegration (Termoskan-2 device, SPA Analitpribor, S.-Peterburg). Parameters: temperature of the beginning of intensive exothermic decomposition (t_b); growth rate of the differential temperature (v^t); characteristic to temperature of exothermic peak (t_{peak}) and its intensity (h_{peak}); relative coefficient of thermal emission of system (K), which is calculated as the ratio of the area of exothermic peak of system to the area of peak nitrate ammonium. Results of thermal researches are given in Table 1.

Table 1. Nature of thermo-decompounding of the stoichiometric mixtures “ammonium nitrate — combustible component”

System	T_b, ^0C	v_t, grad/(min)	T_{peak}, ^0C	H_{peak}, ^0C	K
Ammonium nitrate (AN)	230	1,47	276	2,13	1
AH— diesel gas oil	223	2,8	282	3,05	2,44
AH–industrial oil I-20	250	7,9	290	13,09	3,67
AH– black oil fuel	216	8,95	262	11,79	9,04
AH– paraffin	250	6,6	282	4,19	1,91
AH– ceresine	253	4,2	283	5,66	2,23
AH– wax paraffin oil	255	5,86	290	5,62	2,22
AH– sunflower oil	230	16,7	255	17,7	10,91
AH– linseed oil	216	21,3	248	20,6	11,89
AH– esters of plant oils	204	8,71	257	9,24	8,01
AH- natural boiled oil	216	21,5	245	11,8	14,15

It is established that while transition from oil products to plant oils, level of their influence on thermo-decompounding of the power condensed system increases. At the same time, with increase in degree of unsaturation of the fatty acids which are a part of oils composition, the speed of their oxidation grows. Among the oils containing olein (CI18), linoleic (CII18) and linolenic (CIII18) acid (contain one, two and three unsaturated bonds, respectively), the ratio of speed of oxidation is 1:27:77 [4].

Apparently from Table 1, the relative coefficient of thermal emission (K) of the systems containing plant oils (sunflower and linseed) exceeds a thermal emission of systems with industrial oil and waxes by 3-5 times, and the growth rate of differential temperature – by 2-2,5 times. The maximum intensity of thermal emission is observed in case of natural boiling oil. It can be explained by desiccants (salts of cobalt, manganese and lead with resin acids) in drying oil; they are catalysts of the radical mechanism of oxidation of unsaturated hydrocarbons [5].

As it follows from the provided data, it is necessary to use linseed oil and natural drying oil as a fuel phase for obtaining of the elementary ammonium nitrate ES. However, because of high viscosity of these products (20-30 mm^2/s),exceeding much viscosity of diesel fuel, the attempt of achievement of uniform distribution of combustible component on the whole surface of granules of ammonium nitrate (AN) and throughout the volume of ES was not successful.

The problem was solved due to use of mix of esters of vegetable oils, vegetable oils and desiccants (naphthenates and oleates of transition metals) as a fuel component of granulated by ES. The similar fuel phase possesses the high speed of oxidation and provides sufficient intensity of thermo-decompounding of system that improves its detonation characteristics. It was confirmed also by experimental measurements of delay of autogenous ignition; presence of up to 1% of desiccants in composition of combustible phase provided decrease in specified effective energy of activation of thermo-decompounding of system by 2-2,5 times.

The explosive substance obtained on the basis of the granulated ammonium nitrate and developed fuel phase has obtained the name Ukrainit-ANFO (Pat. UA 79813, UA 85959).

The technology of obtaining the highly stable granulated ES assumes increase in absorbing ability of granules of ammonium nitrate in relation to liquid fuel from 2,0-2,5% up to 7,5-9,0% of mass. The created technology excluded use of porous ammonium nitrate which is not produced in Ukraine. Moreover, the majority of low-density ammonium nitrate produced abroad along with the high absorbing ability possesses low mechanic-strength characteristics that leads to blocking of charging hoses when pneumo-transporting and charging of ES.

On the basis of systematic experimental work on modifying of AN granules, the unique technology of porization of agrarian granulated ammonium nitrate (grade B) in case of maintenance of sufficient strength of granules has been developed.

The technology assumes processing of AN by pore-forming solutions of salts of ortho-phosphoric acid and subsequent heating in special vacuum mixers at a temperature of 60-65^{0}C and negative pressure of 0,7 ÷ 0,9 atm. The hot modified nitrate is mixed with the esters of fatty acids of plant oils and/or vegetable oil containing oxidizer catalysts, namely, fat-soluble salts of transitional metals (Pat UA 106118).

Solutions of salts of ortho-phosphoric acid not only wash away free flowing agents(decomposition phlegmatizers) from a surface of AN granules and conduce pore formation, but also increase granules strength. Mechanic-strength characteristics of granules are improved due to formation of reinforce frame from compounds slightly soluble in water. These compounds are phosphates of alkaline-earth metals which are a part of the conditioning additives of granulated AN. The granules obtained as a result of modification of AN possess highly-developed surface, which allows holding up to 7,5–9,0% of mass of liquid fuel, also possess sufficient strength. This technology was successfully implemented in granulated ammonium nitrate of all the Ukrainian producers, and also KazAzot LLP (Kazakhstan), JSC Maxam-chirchiq and JSC Farg'onaazot (Uzbekistan), JSC Minudobrenie (Rossosh, Russian Federation), AZ “Pulawy” (Poland).

The technology and composition of the granulated trotyl-free explosive substances of factory production of Ukrainit-ANFO have no analogs among the known systems of this kind. Ukrainit-ANFO is well-balanced on fuel almost in each granule of ES, does not possess the obvious smell of oil products, has guarantee period at least 3 months, removal of combustible component from surface of granules is not observed in case of pneumocharging. Detonation characteristics of Ukrainit-ANFO allow effective use of it for pneumatic charging of hole and wells of small diameter. Industrial production of Ukrainit-ANFO is implemented in the production site PJSC “Promvzryv” (Zaporizhzhia). Developed ES is successfully used for pneumocharging of holes and wells in mines PJSC “Zaporizhzhia iron ore plant” and PJSC “Evraz Sukha Balka” in amount up to 250 tons a month.

Table 2. Physical and chemical characteristics of ES Ukrainit-ANFO

Index	Norm
Oxigen balance, %	- 0,1 ÷ -1,7
Heat of explosion, kJ/kg	3760 – 3820
Gases volume, l/kg	980 – 990
Speed of a detonation, km/s: – in a steel pipe	3,2 – 3,8

Critical diameter of detonation of an open charge, mm	35-40
Sensitivity to blow in shock machine K-44-II: – the lower bound at P = 10 kg, mm – frequency of explosions at P = 10 kg, N = 250 mm, %	 500 0
Sensitivity to friction (lower bound) in shock machine K 44-III, MPa (kgf/cm^2)	≥ 702 (≥ 7020)
Transition from deflagration to detonation in open volume	Impossible
Amount of harmful gases of explosion in conversion to relative CO, l/kg	28 – 40

Technology of cartridged of emulsion ES Ukrainit-P.

The cartridged emulsion explosive substances (ES) should not be exceeded in working capacity and universality, and should exceed considerably standard cartridged ES Ammonite No 6ZhV in safety of application. Moreover, cartridged emulsion ES should possess steadiness (for manual charging of holes) and long (not less than 6 months) holding of physical stability and high detonation parameters for use in underground mines of Ukraine.

As it is known [6-7], the inverted emulsions of the high-concentrated oxidizer solution (91-93% of mass) in the hydrocarbonic medium (7,0-9,0% of mass) are the basis of EES. It is established that the majority of EES properties are determined by dispersion of emulsion, with which growth the interphase surface "oxidizer / fuel" is increased that provides high sensitivity and detonation characteristics of system [5]. However, with growth of dispersion the thermodynamic probability of destruction of emulsion also increases.

Obtaining of stable cartridged ES with high detonation parameters can be provided only by scientific-based approach to the solution of complex of research tasks: definition of the nature and concentration of an oxidizer phase, fuel phase and emulsifier, technology of emulsification, and sensitization.

Unlike filling emulsion ES where the content of water is 14–18% of mass, in cartridged emulsions this value should not exceed 7–10% of mass. It is caused by effect of water as phlegmatizer due to selection of heat for evaporation from a zone of chemical reaction of explosive transformation (increase of water content in emulsion by 1% of mass leads to decrease in operability of explosive system by 1,7% [8]). However, at the low content of water, the probability of crystallization of nitrate and loss of detonation ability of EES increases in disperse phase of emulsion.

When studying of solubility of ammonium nitrate and its combinations with sodium and calcium nitrate, it has been established that use of AN monosolution requires holding of high technological temperatures of production of EES. During transition to binary systems solution, crystallization temperature decreases significantly. However, use of system ammoniac/sodium nitrate when creation cartridged emulsion substances, it is limited to low solubility of sodium nitrate (176 g in 100 g of water at 100 ^{0}C).

For EES with various composition of oxidizer, calculations of detonation characteristics of EES (perfect speed of detonation, critical diameter of detonation, relative working capacity) have been carried out according to the approximating model [9]. According to the obtained results of system on the basis of binary solution, ammonium/sodium nitrate possesses considerably lower speed of detonation and bigger critical diameter of detonation, than emulsion on the basis of ammoniac/calcic nitrate. The obtained data are confirmed by the results given in paper [10], replacement of a part of ammonium nitrate by sodium nitrate led to decrease in operability of ES by 7,5%.

As a result of researches optimum for cartridged emulsion substances, the following composition of oxidizer has been determined: % of mass, H_2O 7,0-10,0; $Ca(NO_3)_2$ 27,5-31,5; NH_4NO_3 58,5-65,5.

The composition of fuel phase of cartridged ES developed by results of thermal researches and model experiments is based on application of composition of dimeric surface-active reagents on the basis of seed fats in mixture of industrial oil and products of conversion of plant raw materials, and ceresin or oil wax are used as structure additive.

The task of ensuring high dispersion of emulsion and stability of cartridged emulsion ES with the content of water up to 10% of mass has been solved by means of the device of static emulsification of original design (Pat. UA 69553). The device is distinctive in that in one case it combines several operated emulsification stages, and allows obtaining emulsions of the necessary viscosity (more than 103 Pa·s) and dispersions (1,3-3,0 microns).

It is known [6, 7] that emulsion systems are capable to detonate only when intake of hollow microspheres or gas-generating additives which reduce emulsion density. However, the chemical gas generation is successfully used for sensitization of bulk EES and is almost not applicable for cartridged EES with long storage time. Proceeding from it, sensitization of cartridged emulsion was performed by input of hollow microspheres (polymeric or glass).

By results of comparative polygon testing of EES sensibilized by microspheres of various producers and various chemical nature, the following results were obtained. The systems with glass microspheres K1 of 3M grade possess best sensitivity and shattering effect (the true density is 0,12-0,14 g/cm^3, average diameter of particles is about 100 microns). Also, rather good results were obtained in glass microspheres Q-Cel 6014k of Potters Industries LLC (true density is 0,13-0,19 g/cm^3). However, higher density of these microspheres in comparison with K1 requires increase in their contents in an emulsion from 3,0% of mass up to 3,8-4,5% of mass that significantly reduces volume concentration of energy of ES. Mikrosfera Q-Cel 7019k (true density is 0,19-0,25 g/cm^3) and polymeric microspheres PSV-15 and PSV-25 are weakly applicable for sensitization of cartridged ES.

The obtained results provided the basis for cartridged emulsion ES of grade Ukrainit-P [11]. In case of blast-hole breaking, industrial tests of this ES have shown that Ukrainit-P is not exceeded in operating capacity, and exceeds Ammonite No 6ZhV in safety of explosive products. However, increased consumption of Ukrainita-P (for 30-40%) was noticed in comparison with Ammonite No 6ZhV when crushing of oversize material. It required additional researches on increase in operating capacity.

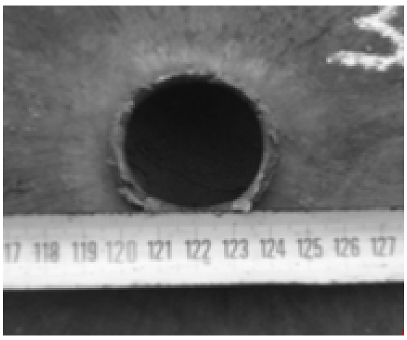
Ammonite No 6ZhV possess the increased working capacity due to combination of high level of heat of explosion Q = 4312 kJ/kg and speeds of detonation D ≤ 4,8 km/s. At the same time, the emulsion ES containing up to 10% of mass of waters cannot possess the explosion heat higher than 3400 kJ/kg at rather high speed of detonation D = 4,7-5,1 km/s.

For increase in heat of explosion of ES, energy additives are usually introduced into composition, for example aluminum powder. However, according to modern standpoints [3, 12], aluminum reacts not with ES components, but with explosion products by Chapman-Jouget plane, and energy of such interaction raises only high-explosive component of explosion without supporting the detonation front. It leads to reduction of speed of detonation and percussion action of explosion.

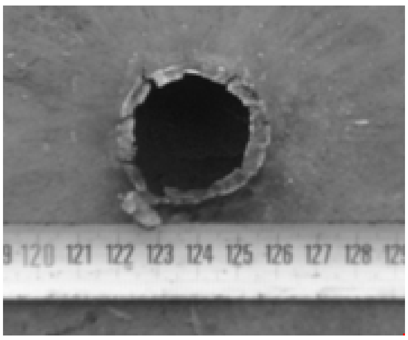
The task of increase in EES power parameters at maintenance of high speed of detonation has been solved due to joint introduction of powder of PA-4 aluminum with the high content of active aluminum and liquid chlorinated paraffin wax to the emulsion.

In literature [6], it is mentioned that chlorinated paraffin wax in small amounts (up to 1% of mass) can have the sensibilizing effect on emulsion systems. It has been confirmed with results of the differential and thermal analysis, introduction of 1% of mass of liquid chlorinated paraffin wax reduces the characteristic temperature of decomposition of emulsion by 12 degrees, at the same time, increasing intensity of system decomposition. It can be explained with decomposition of chlorinated paraffin wax at temperatures over 150^{0}C with formation of HCl [13] which has catalytic effect on thermo-decompounding of ammonium nitrate [14]. Chlorinated paraffin wax as a part of EES accelerates reactions of explosive transformation and provides increase in temperature in a zone of chemical reaction that leads to growth of speed of ES detonation and percussion action of explosion.

Cartridged ES with explosion heat of 3900-4300 kJ/kg and speed of detonation of 4,9-5,1 km/s were obtained by joint introduction of chlorinated paraffin wax and powder of highly active aluminum to the emulsion. Results of comparative tests of shattering effect of Ukrainita-P (with aluminum) and Ammonite No 6ZhV are given in Figure 1. Shattering effect was evaluated by penetration into steel plate with thickness of 12 mm.



1)



2)

Figure 1. Comparative tests of shattering effect: 1 - cartridged Ukrainit-P; 2 – trotyl-containing ES Ammonite No 6ZhV

According to results of conducted researches, composition and obtaining technology of cartridged emulsion ES Ukrainit of grades P-S, P-SA and P-P were developed. Ukrainit-P-P is intended for blast-hole charges formation, and Ukrainit-P-S and P-SA can be successfully used as an intermediate detonator for initiation of charges of the emulsion and granulated ES in wells and holes of any diameter, and also for crushing of oversize material. High parameters of operating capacity (heat of explosion is 3900-4300 kJ/kg, speed of detonation is 4900-5100 m/s and critical diameter is 20-23 mm) allow production of cartridges of any diameter (from 32 mm), and small amount of harmful gases of explosion (up to 25 l/kg in case of recalculation on AN) reduce toxic impact of personnel. Industrial output of cartridged ES Ukrainit-P is fulfilled at the production site PJSC “Promvzryv” (Zaporizhzhia, Ukraine). Cartridges Ukrainita-P are applied in shallow mines of Ukraine and can be used as industrial detonators of borehole charges at open works.

The range and technology of developed granulated cartridged ES Ukrainit in combination with filling emulsion ES Ukrainit provide the complex of solution of problem of conversion of underground mines of Ukraine to trotyl-free ES.

References

1. Baron L. V., Kantor V. Kh.(1986) *Tehnika i tehnologiya vzryivnyih rabot v SShA, Moskva, Publishing house: Nedra* [Technique and technology of blasting operations in USA]. Moscow: Nedra, 376 p.
2. Dubnov L. V., Bakharevich N. S., Romanov I. A. (1987) *Promyishlennyie vzryivchatyie veschestva* [Industrial explosives]. Moscow: Nedra, 358 p.
3. Orlenko L. P. (2002) *Fizika vzryiva* [Explosion Physics] Moscow: Fizmatlit, Vol. 1. 832 p.
4. Nechaev A. P. , Traubenberg S. E. , Kochetkova A. A. (2007) *Pischevaya himiya* [Food Chemistry]. St. Peterburg: GIORD. 640 p.
5. Denisov E.T., Afanas’ev L. B. (2005) Oxidation and Antioxidants in Organic Chemistry and Biology. CRC Press, 1024 p.
6. Wang Xu Guang (1994) Emulsion explosives. Beijing: Metallurgical Industry Press, 388 p.
7. Kolganov E. V., Sosnin V. A. (2009) *Emulsionnyie promyishlennyie vzryivchatyie veschestva, Sostavyi i svoystva* [Emulsion industry explosives, The compositions and properties]. Dzerzhinsk, State Research Institute “Kristall”, 592 p.
8. Matorin A. S., Pavlyutenkov V. M. (2004) *Vodosoderzhaschie vzryivchatyie veschestva mestnogo prigotovleniya* [Slurry explosives of local preparation]. Yekaterinburg, Ural Branch of Russian Academy of Sciences, 194 p.
9. Gorinov S. A., Kuprin V. P., Kovalenko I. L, Sobina E, P. (2010) Teoreticheskaya otsenka vliyaniya himicheskoy prirodyi okislitelya na detonatsionnyie harakteristiki emulsionnyih vzryivchatyih veschestv [A theoretical estimate of the effect of the oxidizing agent chemical nature on the detonation characteristics of emulsion explosives]. *Razvitie resursosberegayuschih tehnologiy vo vzryivnom dele* [The development of resource-saving technologies in the explosive industry]. Yekaterinburg: IGD UB RAS], p.p. 191- 201.
10. Kukib B. N. (2012) O vliyanii himicheskogo sostava okislitelnoy fazyi emulsii na skorost detonatsii i otnositelnuyu rabotosposobnost emulsionnyih vzryivchatyih veschestv [On the influence of the chemical composition of the oxidizing emulsion phase on detonation velocity and relative performance of emulsion explosives]. *Vzryivnoe delo* [Explosive industry]. Moscow, JSC “MCS on explosives at AMS”. No 1110 / 67, p.p. 151-163.
11. Kuprin V. P., Kuprin A. V., Rykov S. V., Savchenko M. V. (2011) Patronized emulsion explosive substance “Ukrayinit-P”: Pat 63689 UA: MPK S06V 21/00, 31/02 S06V /. (UA); appl. 23.08.2011; publ. 10.10.2011., Bul No19.
12. Mencassi S., Lefrancois A. (2003) Temperature and Pressure measurements comparison of the aluminized emulsion explosives detonation front and product expansion. Explosives and blasting technique. Netherland: A.A. Balkema Publishers, p.p. 207-213.
13. Oshin L. A. (1978) *Promyishlennyie hlororganicheskie produkty* [Industrial chlorine-organic products] Moscow: Khimiia. 656 p.
14. Glazkova A. P. (1976) *Kataliz goreniya vzryivchatyih veschestv* [Catalysis of explosives combustion] Moscow: Nauka, 264 p.