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TO THE QUESTION ABOUT SAFETY OF TECHNOLOGIES PREPARATION NON-TROTYL EXPLOSIVE SUBSTANCES

Розглянуто проблеми вибухонебезпеки різних типів безтритилових вибухових систем і причини, що їх створюють. Наведено способи ослаблення чи усунення загальних та індивідуальних причин настання вибухонебезпеки різних вибухових систем.

Ключові слова: безтритилові вибухові речовини, сумішеві речовини, водо вміщуючи, емульсійні, добавки, детонаційні показники.

Рассмотрены проблемы взрывоопасности различных типов безтритиловых взрывчатых систем и создающие их причины. Указаны способы ослабления или ликвидации общих и индивидуальных причин возникновения взрывоопасности различных взрывчатых систем.

Ключевые слова: безтритиловые взрывчатые вещества, смесевые вещества, водосодержащие, эмульсионные, добавки, детонационные показатели.

Considers problems of explosion – prove the difference types phenylmenthan – free explosives Systems and creator them causes. Indicaties fashions of weakening or removal general and individual causes origin explosion hazard difference explosive systems.

Keywords: phenylmenthan – free explosives, non-trotyl explosive substances, trotyl-containing, composite energetic, water – containing explosive, blasting emulsion, coolant, detonating parameters.

1. General actuality of the subject

1.1. Transfer to non-trotyl explosive substances.

Almost all explosive substances (ES) in various industrial areas are compound systems.

Compound systems' operating and explosive characteristics including risk factor (safety) are determined by properties of their components such as their chemical and physical compatibility, uniformity of distribution in each other and by manufacturing processes.

Some systems (“trotyl-containing”) include an individual ES (trotyl, hexogen, octogen etc.) as a basic component. It creates a risk of harmful impact on workers' bodies that can follow negative repercussion on their health and life.

These ES are explosion and fire hazards in case of not following operational procedure. Other systems (“non-trotyl”) exclude the presence of an individual ES that were mentioned previously. The main component here is ammonium nitrate (AN).

Today, non-trotyl explosive systems (ES) become more and more popular. Noticeable the desire to use ES that are cheaper than trotyl-containing ES. As well, the risk of explosion and fire hazards reduces. Absence of contact with an individual ES allows exclude carcinogenic effect on an employees' bodies.

1.2. Types of ES

The biggest part of ES that are used in mining consists of two groups of mixtures and composition from these mixtures:

Ammoniac saltpeter mixtures (AN) as granules. Recently, they are mainly porous(PS), with multiple combustible additions in various aggregate states (Granulites and Ihdanites);

The most widespread AN is type of mixtures with liquid flammable additions. More often they are petroleum products, diesel fuel (DF) for example. These mixtures are known under the general name – Ihdanites or AN – DF type of mixtures;

Mixtures that are based on water solutions of AN and other salts oxidants (nitrates), having the generalized name water-containing ES.

2. Safety issue in ES manufacturing process.

2.1. General and individual problems with various ES.

2.1.1. Ihdanites or AN – FO type of mixtures.

Compound ES with the ammoniac saltpeter base (crystalline, powdery or granular) are made by mechanical mixing of components: AN and combustible additions (one or a few). Can be used any of the known methods, including manual, that provides efficiency and safety of process.

High quality ES with an excellent explosive characteristic can be made by using special brands of raw materials and without any auxiliary technique or additions for initial components preparation and mixing.

Should be noted that special brands of raw materials or raw materials with necessary quality for making different types of compound ES are not produced in Ukraine. First of all it refers to ACE as the main component of compound ES by the volume of applications.

Well known that properties, processing characteristics and efficiency of application of the mixed ES significantly depend on a type (production form) and quality of ACE. In mixtures of ACE in the hard state with combustible additions, first of all with liquids, the most effective is a form ACE as porous granules [1].

Let's look at ES “Ihdanite”, which is mixture of granular ammoniac saltpeter with diesel fuel and is prepared in place of application.

The explosive effect of Ihdanite's charge on environment is big due to the significant magnitude (in comparison to powdery mixtures and individual explosive connections) of chemical reaction zone, impulse width and critical diameter of charge. These parameters are stipulated by compound (two-phase) mechanism of chemical transformation that proceeds in every concrete moment at interface between components - on the surface of each granule.

Maximal freeing of explosion energy of ES with the concrete incorporated into the system potential is conditional. That is real when the final products of the reaction are oxides with the highest oxidation state of elements from the initial explosive system.

Since the considered ES is a compound system then composition of final products of explosive decomposition depends on the completeness of processes on both its stages, that is determined by both reactionary ability of components and equipartition of their decomposition's products in the gas phase. The last one strongly depends on even distribution of oxidant and combustible components in the explosive compound system. The task of equal distribution of components in the volume of the system is unsolved for Ihdanite. The system is physically unstable; the fuel is flowing down to the underneath of a charge. At such exfoliation the system is characterized by instability of detonation indexes.

2.1.2. Water-containing ES.

These are mixtures with various chemical and physical structure that determined by specific manufacturing process. There are a few types of these mixtures with different technology of production, and the most important thing - with different physical and chemical structure: gels, emulsions and/or "direct" type suspensions, "reversal" type emulsion. The most distributed ones are the emulsions of "reversal" type, known under the general name – emulsion ES (EES).

High working capacity and controllability of detonation indicators against the background of water resistance and stability of systems is achieved by creating a water-containing systems (water-gel, water-emulsion). Solutions with high concentration of AN or eutectic mixtures of ammonium, sodium, calcium nitrates and urea are used there as oxidants. High-temperature technologies are used to eliminate crystallization and increasing the viscosity of the concentrated oxidant solution.

Eutectic mixtures help increase fluidity of ES because of lower crystallization threshold than ammonium nitrate has. However, they decrease irreversible losses of the thermal energy of explosion for the heating of solid calcium and/or sodium oxides that appear in the detonation products.

Water-emulsion ES (WEES) is high concentrated reversal "water in oil" type of emulsion.

Dispersed phase is a solution of the oxidant and dispersive medium is hydrocarbon fuel in mixture with the emulsifier. The production process of WEES includes using of AN, calcium nitrate, products of oil refining, water, hollow spheres, gas bubbles, emulsifier.

Components preparation includes the following steps. First, receiving and storage of concentrated water solution of oxidant at 90°C. Second, piping of this oxidant to a mixer, where it is mixed with the required strictly standardized amount of fuel and emulsifier that come from separate tanks. As a result, an oxidizer's matrix is formed - emulsion "oxidant in fuel". The matrix is pumped through a pipeline to a mixer, where it is aerated by an agent (hollow microspheres, gas bubbles) and acquires the properties of an explosive substance. Aeration of the matrix sensitizes the system, or in other words it increases its sensitivity to the initiating impulse.

We can get highly sensitive or low sensitive to the initiating impulse WEES using different dosage of the sensitizer and its dispersion. Emulsion formation is carried out by mixing, colloid grinding and homogenization.

Emulsion as ES matrix has to be characterized as a fairly stable non-explosive system. However, nitric acid formed as a result of hydrolysis of AN ($\text{MH}_4\text{M0}_3 + \text{H}_2\text{0} = \text{NH}_4\text{OH} + \text{HNO}_3$) increases sensitivity of matrix to the initiating impulse, sensitizes it and provokes an unauthorized explosion. As it happened with a poremite matrix at Kalinovskiy chemical plant in Russia [2].

The usage of calcium nitrate in ES Ukrainit-D neutralizes environment (pH = 7,2), that decreases dangerous of premature sensitization..

Detonation sensitivity of WEES is provided by solid, liquid and gaseous sensitizers. Powders of aluminum, silicon, ferrosilicon, silicocalcium, microspheres with gas-air filling, porous expanded materials (silica, vermiculite), gas-generating powder additives are input into WEES for the purpose of sensitization.

Solid powder aerators provide stability of WEES detonation properties. Material's phase transitions in hollow gas-filled aerators take heat from the reaction zone. Gas-generating additive destabilizes the detonation process due to the uncontrolled aerating process.

Design of the WEES preparation unit should ensure compliance with the temperature regime determined by the recrystallization temperature of the oxidant. It should prevent the formation of stagnant zones, prevent aerating at the stage of matrix formation, exclude air sucking (perfect mixing in a vacuum), safety of pumping of finished products through the pipelines.

The danger at the stage of matrix preparation is a not prescribed by regulations increase in its sensitivity. This happens due to self-aeration of the matrix by the air-gas mixture in the case of sucking air into the system and/or using low-boiling hydrocarbons generating gas

The danger at the pumping stage is explained by the fact that in case of not following the mixture recipe while preparation, the sensitivity of the WEES increases. For example, a slight decrease of water volume in the matrix mass can at any time lead to detonation of the system.

Moreover, non-compliance with the temperature regime promotes the formation of stagnant zones and plugs.

To avoid self-aeration of the WEES matrix, the mixer must work with counterpressure and be a closed system [3, 4]. In order to achieve the regulated sensitivity of the finished product in the process of aeration, it is necessary that the rate of oxidizer supply to the fuel and the optimal emulsification time in the mixer strictly comply with the technological regulations.

2.2. Causes creating explosive problems ES

There is one general problem for Ihdanites and WEES - Instability of detonation parameters.

Instability of the detonation parameters for Ihdanites is the result of uneven components distribution in the mixture combined with background of physical instability. Its main reason should be considered the low absorbing and retaining capacity of AN pellets (domestic raw materials) in relation to diesel fuel.

Eutectic mixtures help increase fluidity of ES because of their lower crystallization threshold than AN. However, their weakness is irreversible loosing of part of explosion energy as it was mentioned previously.

Emerged unauthorized increase in the WEES system sensitivity is determined by:

- self-aeration of the matrix by the air-gas mixture in the case of sucking air into the system and/or using low-boiling hydrocarbons generating gas as a fuel;
- formation of nitric acid as a result of hydrolysis of ammonium nitrate while the matrix is sensitized (danger of explosion);
- non-compliance with the formulation of the mixture, for example, a slight decrease of water volume in the matrix mass increases the sensitivity (danger of detonation)
- rate of oxidizer supply to the fuel and the optimal emulsification time in the mixer do not comply with the technological regulations;
- destabilization of the detonation process by a gas-generating additive due to uncontrolled aerating process.

3. Ways to ensure the safety of the preparations ES

For Ihdanites

3.1. Additives. Inclusion in the composition of solid fine-divided combustible additives such as aluminum powder, microfine stone and charcoal, wood sawdust, etc., well adsorbing liquid components. Provision of optimal surface contact of fuel and oxidizer, increase of volumetric energy concentration is achieved in metallized Ihdanite due to the use of disperse aluminum and surfactants.

3.2. Preparation modes. Preparation of component AN. Porosity AN by heat treatment - heating (cooling) to temperatures exceeding the temperature of phase transitions. When the AN is taken as a finished granule, the changes occurring in the structure can be defined as the formation of cracks in the crystalline blocks and the yield of these cracks on the surface of the granules and cavities in them. This leads to a change in the nature of the porosity from the "closed" to the

"open", increasing the homogeneity of the distribution of the cavities, including cracks in the granule. As well, it creates the disruption of the uniformity of the surface of the granule and to the reduction of the bulk density by 5-10% [5, 6, 7].

To avoid increasing the sensitivity of the WEES system is recommended:

3.3. Eliminate the intake of air into the system and the use as fuel of low-boiling hydrocarbons that generate gas.

3.4. Use of calcium nitrate to reduce the risk of premature sensitization.

3.5. Compliance with the formulation of the mixture, the water content in the matrix mass to avoid unauthorized sensitization WEES.

3.6. Mixer must work with counterpressure and be a closed system. The rate of oxidizer supply to the fuel and the optimal emulsification time in the mixer must strictly comply with the technological regulations.

3.7. Stabilization of the WEES detonation process with the exception of the gas-generating additive from the mixture's formulation because of the uncontrolled aerating process.

Conclusions

1. Preference for non-trotyl explosive systems allows:

- use them as cheaper option than ES with trotyl-containing;
- reduce the risk of explosion and fire hazard of the process by excluding from the system individual components ES;
- absence of contact with individual explosives excludes their carcinogenic effect on the body of workers.

2. Of non-trotylic ES, the most common are:

- mixtures of AN with liquid combustible additives, more often oil products, for example, diesel fuel (ihdanites);
- mixtures that are based on water solutions of AN and other salts oxidants (nitrates), having the generalized name water-containing ES. The most widely used emulsions of the "reversal" type, known under the general name of emulsion explosives.

3. The general problem of the safe preparation of various ES is the instability of detonation parameters.

For ihdanites: the instability of the detonation parameters of the ES is due to the uneven distribution of components in the mixture volume along with the background of physical instability. The main reason for this has to be considered the low absorbing and retaining capacity of AN pellets (domestic raw materials) in relation to diesel fuel.

For WEES: the reason of instability is the reduction of the energy potential in ES due to irreversible losses of a part of the explosion thermal energy on the heating of solid oxides of calcium and / or sodium that appear in detonation products.

4. Individual safety problems in SS manufacturing process.

There is an individual increase in the sensitivity of the system for different WEES, which is determined by:

- self-aeration of the matrix by a gas-air mixture in the case of sucking air into the system and / or using low-boiling hydrocarbons generating gas as fuel;
 - formation of nitric acid as a result of hydrolysis of ammonium nitrate;
 - non-compliance with the formulation of the mixture (a slight decrease in the water content of the matrix mass);
 - preparation modes do not comply with the technological regulations;
 - destabilization of the detonation process by the gas-generating additive due to uncontrolled aerating process.
5. Ways to ensure the safety of ES preparation:
- for ihdanites. Optimal surface contact of fuel and oxidizer by adding additives;
 - special preparation of AN by porosity;
 - for WEES. Exclusion from the mixture gas-generating additives due to uncontrolled aerating process;
 - the recipe and preparation regimens must comply with the technological regulations.

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