Research of pyrophoric compounds in order to reduce their hazard

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The constantly growing content of sulfur compounds and the increased water content in the extracted oil enhances the aggressiveness of the environments in which the technological equipment of oil depots and pipelines operates, resulting in a higher number of emergencies in the equipment of oil refineries. Thus, one of the most urgent problems is the corrosion damage to oil storage equipment and the associated consequences of flammable pyrophoric compounds formation.

Finely dispersed flammable sulfides with organic impurities are formed in the equipment of the diesel fuel distillate hydrotreating unit thus accumulating on the bottoms and walls of tanks and reservoirs. This negatively affects the material balance of the hydrotreating process and increases fire and explosion hazards of the whole hydrotreating process at the refinery. For the first time, the elemental composition of pyrophoric deposits formed while storing petroleum products in the LCh-24-2000 unit was experimentally investigated. These sulfides are a flammable component of the equipment in the hydrotreating process, where diesel fuel distillates rotate.

The obtained results of the test study as for the prevention of pyrophores spontaneous combustion indicate that hydrogen peroxide solutions have the highest efficiency. The practical significance of the results is in the use of experimental studies on the spontaneous combustion of pyrophoric samples in the development of the equipment cleaning terms during the hydrotreating process from pyrophoric deposits at the refinery. The experimental results of testing the ability of chemicals to prevent pyrophores spontaneous combustion can be used to reduce the risk of spontaneous combustion of pyrophoric compounds.

1. Introduction

Fires at the enterprises of production, storage, refining and transportation of oil are a global problem [1, 2]. The biggest number of all the fires occur in oil supply facilities - 54% and refineries - 25%.

The main factors and the main reasons contributing to the occurrence and development of probable emergencies at refineries are: equipment failure (corrosion, wear of parts and gaskets, deformation, expiration of term service); operation of non-sealed equipment; irregularity and low quality of maintenance; violation of the modes for the liquids pumping process (pressure, temperature, pumping speed); staff errors due to low-quality training or lack of experience; external factors (fires at neighboring facilities, traffic accidents).

According to the data [3], the constantly growing content of sulfur compounds and the increased water content in the extracted oil enhances the aggressiveness of the environments in which the technological equipment of oil depots and pipelines operates. Therefore, one of the most urgent problems is the corrosion damage to oil storage equipment and the associated consequences of flammable pyrophoric compounds formation.

A significant number of emergencies in the equipment and storage tanks for high-sulfur oil and petroleum products was due to the ignition occurrences of pyrophoric deposits [3, 4]. Thus, the solution to this problem may be connected with the development of innovative methods and means of phlegmatization of pyrophoric deposits, cleaning them from the inner surface of the equipment tank for petroleum products storage.

2. Analysis of literature data and problem statement

Pyrophoric deposits are formed owing to the corrosion processes on the inner metal surface of the equipment due to the chemical reaction Fe + S = FeS + FeS_2 as well as iron sulfides FeS containing iron oxides Fe_2O_3 and Fe_3O_4 and free sulfur.

Thus, the authors [5] established the composition of pyrophoric compounds and synthetically obtained iron sulfide, simulating the formation of pyrophoric compounds. The synthetic sulfide is characterized suing spectral and thermal analysis, electronic probe. The authors' data indicate a low degree of crystallinity and easiness of self-heating and spontaneous combustion of the synthetic iron sulfide.

Self-ignition of pyrophoric compounds in air can take place at both above-zero and sub-zero temperatures and occurs due to self-heating of wet pyrophoric deposits up to the temperature of 180 ... 220 °C, free sulfur, which corresponds to spontaneous combustion, provokes gas ignition. The activity of pyrophoric compounds increases with the growth of the environment temperature [4, 5]. The authors [6] studied the pyrophoric tendency of corrosion products in tanks with petroleum products. The pyrophoric compounds were heated up faster at the temperature below 250 °C with the critical thickness of corrosion products less than 10 mm.

The danger of corrosion of the tanks inner surfaces is not only in the various perforations and corrosion cracking of the tanks walls and bottoms, but also in the possibility of oil and petroleum products ignition due to the exothermic corrosion reactions. Such reactions include the interaction of the exposed iron surface and its sulfides – the pyrophoric compounds with the oxygen in the air. The probability and intensity of these reactions increase sharply when the corroding or corrosion coated products contact the air. Such conditions occur while emptying the equipment and tanks, when their walls directly contact with oxygen [3, 4].

The authors [7] identified possible causes of the increased corrosion wear of pipe bundles of heat exchangers, in which pyrophoric compounds are formed. The most typical kinds of damage to the heat exchanger pipes are shown, depending on the operating conditions. Recommendations aimed at reducing the corrosion wear of pipe bundles for typical operating conditions at refineries are given.

The authors' research [8] on pyrophoric deposits allows to give some practical recommendations for chemical decontamination of pyrophoric deposits in the equipment of distillation columns. Such deposits are formed between the plate and the coke layer.

The mechanism of pyrophorically activated metal combustion is quite complicated, and is a complex problem [9] that needs to be solved. As soon as the pyrophoric activated metal is activated by air oxygen, oxygen diffuses into the activated metal in large quantities and reacts with it, which increases the contact area with oxygen [9]. Therefore, the solution to this problem may be connected with the development of innovative methods and means of pyrophoric deposits phlegmatization, cleaning them off the inner surface of the tank equipment for petroleum products storage. Various methods are used for the equipment to be protected against the pyrophoric compounds formation [10]. The invention represents a thin film-forming raw material with and is used for the equipment surface treatment. The authors [11] studied the processes of pyrophoric deposits formation in various industries. In the context of the dangers of iron pyrophoric sulfides, the existing methods and means of decontamination of these compounds are analyzed.

The depth of distillates hydrotreating from sulfur and other compounds depends on the type of hydrocarbon feedstock, process temperature, hydrogen partial pressure and its circulation rate, volumetric feed rate, material balance and other factors. Therefore, the main controlled parameters of hydrotreating are: temperature, volumetric feed rate, pressure, rate of circulation of hydrogen-containing gas, hydrogen content, material balance of the process [12, 13]. Material balance is an important technological parameter of the distillates hydrotreating process of diesel fuel. Due to the violation of the material balance, the concentration of raw feedstock may be lost due to the formation of flammable and explosive pyrophoric compounds in the equipment and tanks [10, 12]. Experimental studies of the elemental composition of these hazardous substances and options for reducing their hazard are further described in the paper.

3. The purpose and objectives of the study

The aim of the work is to study pyrophoric deposits in order to reduce their danger at the Lysychansk refinery plant LCh-24-2000, which is operated in aggressive environments.

To achieve this goal the following tasks were to be solved:

- to investigate the elemental composition of pyrophoric deposits formed while storing petroleum products in the unit;
- to test the ability of chemicals to prevent pyrophores spontaneous combustion.

4. Materials and research methods of pyrophoric deposits in order to reduce their hazards

4.1 Study of pyrophoric deposits samples

Samples of pyrophoric deposits of LCh-24-2000 unit of Lysychansk oil refinery were used in the work. The method of atomic absorption spectroscopy was used to analyze the composition of the samples (two parallel measurements) of pyrophoric deposits of tank 5 with diesel fuel (Table 1). The studies were conducted using a Hitachi Z 8000 with an H6A-600 electrochemical atomizer. Sample preparation was performed according to the set guidelines [14]. Reproducibility of the measurements is characterized by standard deviation values of 0,2%.

4.2 Prevention of pyrophoric compounds spontaneous combustion

In this work, the prevention testing of pyrophoric compounds spontaneous combustion in the studied system was carried out. The idea of preventing pyrophores ignition by neutralizing them with oxidizing solutions was the basis of the express testing technique in this work. In practice, to prevent spontaneous combustion of pyrophoric deposits, the method of their phlegmatization is widely applied, which consists in wetting the samples of pyrophoric deposits with water in order to prevent interaction with oxygen [12]. However, it does not provide fire safety at the site, as pyrophoric deposits are insufficiently wetted with water, dry quickly and become re-ignitable.

These studies allowed to determine the minimum concentration of the oxidant in the washing solution, at which the self-heating rate of the test sample of pyrophoric compounds obtained from the equipment does not exceed 1 deg / min, which prevents its further ignition. The hydrogen index of the neutralizing solution was determined using a ANION-4 pH meter type. The relative error of measuring the pH values was 0,1 %. The universal device RNT-027 was used to measure the redox potential, specific conductivity, mineralization and water temperature. The relative measurement error of the corresponding parameters was also 0,1 %.

The composition of the neutralizing solutions was developed experimentally. At the initial stage of testing, the prevention of pyrophoric deposits ignition was achieved by the following stages. At first, the samples of pyrophoric deposits heated to a temperature of 60-80 ° C were washed with water containing a surfactant for emulsification of hydrocarbons and their removal, as the conventional steam treatment promotes spatial oxidation of hydrocarbon molecules and pyrophores, which strengthen the deposits layer. [15]. Next, the dispersion procedure of sediments containing hydrocarbons and pyrophores was performed so as to expand the surface area of the latter and increase the oxidation rate of pyrophores. The dispersion was carried out mechanically - under a strong stream of water, as well as with the help of scrapers, and chemically – using dispersants, which create a similar electric charge on the surface of sediment particles, which leads to their mutual repulsion. This was followed by the neutralizing process of deposits which are dispersed with an aqueous solution containing an oxidizing agent. Then the neutralized pyrophoric deposits and those left intact were washed out of the equipment with a large amount of water.

In the laboratory experiments, the effectiveness of the neutralizing chemical compositions was estimated by the number of spontaneous combustions of pyrophoric iron samples in contact with the air. Aqueous solutions of hydrogen peroxide and potassium permanganate were used as the oxidizing medium.

To determine the neutralization efficiency (phlegmatization) of pyrophores, different amounts of oxidants aqueous solutions were added to their samples and the resulting precipitate was dried. The precipitate was then emptied onto a sheet of filter paper and the paper ignition was recorded.

5. The study results of pyrophoric deposits samples

Pyrophoric deposits are studied in order to reduce their danger in the LCh-24-2000 unit, which is operated in aggressive environments.

The object of the study are pyrophoric compounds samples, which were taken from the tank 5 with the capacity of 500 m^3 after cleaning in the diesel fuel hydrotreating unit of Lysychansk oil refinery. The samples for the study were taken with a special sampler made of intrinsically safe material according to the guidelines [3]. To do this, the scraping of deposits from the inner surface of the walls of the equipment above the level of the diesel fuel distillates (two samples) was conducted. The selected brown powder samples were packed in airtight bags to preventing contact of the pyrophoric deposits samples with oxygen. The data as for the type of tank, the composition of petroleum products, the quantitative content of sulfur, as well as the information about the last cleaning of the equipment were monitored.

6. Discussion of the study results of the pyrophoric deposits samples to reduce their danger

6.1 Study of the elemental composition of pyrophoric deposits

Pyrophoric deposits are a mixture of products of hydrogen sulfide corrosion of metal, mechanical impurities, resinous substances and other ingredients of organic origin. The studies by the authors [4] have shown that iron sulfides are formed by the action of hydrogen sulfide not to the iron, but to the products of its corrosion. The pyrophoric deposits, which are formed while storing dark oil products containing elemental sulfur and hydrogen sulfide, are the most activity. Cases of spontaneous combustion of petroleum products pyrophoric deposits are more often observed in the tanks with diesel fuel obtained in the process of primary distillation of sulfur-oils and high-sulfur oils.

Table 1 shows that the content of sulfur and iron in samples № 1,2,3 differ significantly, probably due to the chemical inhomogeneity and the complexity of the content of the elements in the studied pyrophoric sediments.

Table 1

The results of the elemental analysis of pyrophoric deposits in the hydrotreating equipment

Sample No	Element concentration, [%]				
	Fe	S	O	C	H
1	99,1	73,4	0,9	4,3	0,9
2	99,3	72,6	0,8	4,3	0,8
3	98,6	52,0	0,6	7,2	0,9
4	98,8	54,6	0,7	7,5	0,7

The ability of pyrophoric deposits to ignite spontaneously depends on their composition and location of deposits, as well as the environment temperature. The porous structure of pyrophoric deposits and impurities of organic substances contribute to their rapid oxidation. It should be mentioned that pyrophores spontaneous combustion is possible even at low temperatures. Thus, there are cases of their spontaneous combustion at the air temperature of minus 20 °C. This is due to the fact that pyrophores have low thermal conductivity [15], and the amount of heat released during the initial slow oxidation is accumulated in the entire volume of sediments, which results in their self-heating to a flammable temperature.

The obtained data show that the samples differ significantly in the content of sulfur and iron, which is due to the heterogeneity of the pyrophoric compounds composition. The analysis of pyrophoric samples from other tanks confirms this conclusion. If we assume that the main component of pyrophoric deposits is exclusively iron sulfide (Fe_xS_y), then the results of the research show that the sulfur content is approximately 1.1 times higher than theoretically possible, which indicates that the sample contains elemental sulfur. The samples of pyrophoric deposits are a multicomponent mixture of substances and contain other components including elemental sulfur, besides iron disulfide (FeS_2) and sulfur sulfide (FeS).

Therefore, in the oxygen-free environment of equipment and tanks with diesel fuel after its cleaning at the hydrotreating unit, sulfides of different dispersed composition with organic impurities are formed and accumulate on the bottoms and walls of tanks. These sulfides are flammable components of diesel fuel distillates [1, 3, 16].

6.2 The ability of chemicals to prevent pyrophores spontaneous combustion

The results of the research testing as for the prevention of pyrophores spontaneous combustion are presented in table 2. They show that the solution of hydrogen peroxide is most effective in fighting spontaneous combustion of pyrophoric deposits samples. According to the data [15], very often pyrophoric deposits from other sampling sites, in contrast to those selected by us from certain tanks and equipment, have a denser structure and complex composition. Therefore, for further research, the concentration of the detergent ingredient was determined, which increases the penetrating ability of the oxidizing solution and allows to neutralize (phlegmatize) rather thick layers of pyrophore deposits.

Table 2

Oxidants effectiveness for prevention of spontaneous combustion of pyrophoric compounds samples

Sample No	Oxidant	Concentration on solution, [%, mas]	Solution-sample pyrophore ratio	Spontaneous combustion presence
1	$KMnO_4$	1,0	1 : 1 5 : 1	yes not
2	H_2O_2	2,0	1 : 1 5 : 1	yes not

After drying the pyrophoric deposits samples, bringing them to room temperature and emptying them on the filter paper, the pyrophores were heated to the temperature of 80-120 °C, which was recorded using the "Thermoscope-300-1C" pyrometer type.

The conducted experimental studies as for testing the possibility of pyrophoric samples spontaneous combustion indicate the greatest effectiveness of hydrogen peroxide for this solution.

The practical significance of the obtained results is in the possibility to use the experimental studies on the pyrophoric samples spontaneous combustion in the development of the terms for cleaning the hydrotreating equipment from pyrophoric deposits. The experimental results of testing the ability of chemicals to prevent pyrophores spontaneous combustion can be used to reduce the risk of pyrophoric compounds spontaneous combustion.

7. Conclusions

For the first time the elemental composition of pyrophoric deposits formed during storage of petroleum products in the unit was studied. The samples of pyrophoric deposits are a multicomponent mixture of substances and contain, besides iron disulfide (FeS_2) and sulfur sulfide (FeS), other components, including elemental sulfur. Finely dispersed flammable sulfides with organic impurities are formed in the equipment of the diesel fuel distillate hydrotreating unit and accumulate on the bottoms and walls of tanks and reservoirs. This negatively affects the material balance of the hydrotreating process and increases the fire and explosion hazards of the entire hydrotreating process.

Certain test data on the ability of various chemical compositions to prevent pyrophores spontaneous combustion were obtained. In the fight against spontaneous combustion of pyrophoric deposits, a solution of hydrogen peroxide turned out to be the most effective.

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