Selection of the reagent to neutralize hydrogen sulfide and methyl-, ethylmercaptans in oil

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Abstract. Laboratory studies of 2016 on the residual content of light mercaptans at the loading point revealed an excess of the mass fraction of methyl- and ethylmercaptans in the prepared oil of the Borodino field. The studies stated that the most effective results on the residual content of mercaptans in purified oil are achieved by adding the reagent-neutralizer to degassed oil after the second stage of separation. Also, the tests proved that water in oil has an effect on the flow of reaction. The action of the reagent-neutralizer takes place at the “oil-water” phase boundary, the dispersion contributes to the strengthening of mass interchange reducing the response time of the neutralizer with oil. The mode of supply of the reagent-neutralizer should be continuous as when the supply of the reagent is ceased, the process of neutralizing hydrogen sulfide discontinues. The laboratory tests made it possible to select the best neutralizer Desoulfon-SNPCH-1200, to determine its minimum specific consumption and the temperature of heating oil. The application of this reagent-neutralizer will allow doing the effective oil preparation at the loading point of the Borodino field. The amount of Desoulfon-SNPCH-1200 needed to neutralize the mercaptans depends on their content in oil and the required degree of reduction. The usual proportion in processing is 4-5 ppm of Desoulfon-SNPCH-1200 at 1 ppm of mercaptans.

1. Introduction
One of the most important processes related to the extraction, collection, and transportation of marketable oil to consumers – oil refineries – in the preparation of oil in the field [1-5].

The use and selection of the most effective reagents – neutralizers to strip hydrocarbons from mercaptans can improve the quality of marketable oil and improve the environmental situation in fields [6-7].

Modern stringent requirements for the safe transportation and storage of petroleum raw materials, the quality of petroleum products and the transition to high requirements for fuels according to the Euro-4 and Euro-5 standards encourage oil companies to develop and implement new, modern technologies aimed at reducing the content of toxic and corrosive sulfur compounds of oil-hydrogen sulfide and mercaptans [8-11].

The toxic substances contained in oil, hydrogen sulfide and mercaptans, are easily volatile, have an unpleasant pungent smell and must be completely removed from the product for environmentally safe transportation and storage [12].
Sulfur in the Borodino oil field is mainly represented by light mercaptans, so it became possible to remove hydrogen sulfide and mercaptans using reagents-neutralizers. When using neutralizers, a chemical interaction occurs, which results in the formation of inert low-toxic compounds [13-17].

At the same time, neither the reagent itself nor the reaction products should be corrosive and degrade the quality of the raw material. Reagents-neutralizers are introduced into the raw material in small quantities (1-3 kg/t). The main obstacle to widespread use of sinks is their high cost. Therefore, it is important to select highly effective, low-toxic, cheap and stable reagents for storage [18-19].

A wide range of reagents available on the market has shown that the choice of an effective neutralizer for a particular field is made on the basis of laboratory studies and pilot tests. Qualitative evaluation of neutralizers is made on the basis of chemical experiments [20-22].

2. Materials and methods

Laboratory tests allow us to evaluate the comparative effectiveness of reagents. The obtained data are used to determine the flow rate of the neutralizer and the parameters of the oil preparation process for a specific field.

Specific consumption and adjustments to the technological parameters of oil preparation are set in the process of field testing.

Based on the above, a number of laboratory tests were conducted to select a hydrogen sulfide neutralizer for oil at the loading point of the Borodino field [23].

Laboratory studies of 2016 on the residual content of light mercaptans at the loading point revealed an excess of the mass fraction of methyl- and ethylmercaptans in the prepared oil of the Borodino field, the results can be found in figure 1.

![Figure 1. The residual content of light mercaptans in prepared oil in 2016-2017.](image)

Due to the high content of residual mercaptans in oil at the loading point of the Borodino field in 2016, additional laboratory studies were carried out to make a reasonable choice of the most effective neutralizer, and a comparative analysis of tested samples was conducted. The list of neutralizers is presented in Table 1, their physical and chemical properties – in Table 2.
Figure 2. Sedimentation of the products of the reaction between the neutralizer and organosulfur compounds in the oil.

The studies were carried out according to the standard method of the “bottle roll test” at 45°C with various amounts of the reagent-neutralizer by bubbling oil and reagents.

Laboratory tests for the selection of effective reagents-neutralizers were carried out by modeling the process of collecting and preparing oil at the loading point of the Borodino field in two stages.

The effectiveness of the use of reagents-neutralizers was determined by the method of measuring the initial and residual contents of mercaptans as the hydrogen sulfide content in the tested oil of the Borodino field does not exceed the established standards [8].

The first stage determined the amount of reagent required to reduce the mass fraction of mercaptans in oil to levels below 100 ppm, the consumption ratio was considered equal to 2.5 mg/g.

The specific consumption of the reagent was 1.2 kg/t in stripping the oil at the loading point on theoretical values, the maximum time of the effective interaction of reagents with mercaptans was 24 hours. The reagent was mixed with oil using a laboratory shaker [21].

Figure 3. Result of the reaction between the neutralizer and organosulfur compounds with the addition of water.

3 Results and discussion
Given the existing oil preparation technology, which consists of sludging and heating raw oil, the use of neutralizers to remove mercaptans and sulfur compounds is the most effective measure in the current situation. The selection of neutralizers is largely determined by the properties of extracted products including one of the most important qualities of the reagent – the absence of formaldehyde in it [24-25].

The results of studies on the reagents are presented in Table 2. According to the results, it can be concluded that the reagents of Desoulfon-SNPCH-1200, INS-1, and Reaton-21-2 were effective for stripping oil of the Borodino field, the consumption ratios of which were minimal – from 2.3 to 2.5 g/g. The main amount of mercaptans was neutralized within the first 4-6 hours when all the studied reagents were added. During the specified time range, the reduction of the mass fraction of mercaptans
below 100 ppm was achieved only with the addition of reagents Desoulfon-SNPCH-1200 and Reaton-21-2.

Amount of Desulfone-SNPCH-1200 required to neutralize mercaptans depends on their content in the system and necessary degree of their reduction. Usual treatment ratio is 4-5ppm of Desulfone-SNPCH-1200 per 1 ppm of mercaptans.

Desulfone-SNPCH-1200 additionally has protective anti-corrosion effect in hydrogen sulfide-containing environment. The protective effect at dosage of 30g / m³ of liquid is 60-70%.

Reagent also has the properties of bactericide that suppresses growth of sulfate-reducing bacteria. Desulfone-SNPCH-1200 does not adversely affect oil preparation process, quality of commercial oil, and does not contain organochlorine compounds.

At the same time, dosing of reagents Darsan and sulfanox did not allow for mass fraction of mercaptans in oil less than 100 ppm.

Table 1. Neutralizers.

| Neutralizer                          | Manufacturer                  |
|-------------------------------------|-------------------------------|
| Reagent DARSAN (mark N)             | LLC ANK, Ufa                  |
| Specifications 2458-003-50771613-2004, changes NN 1, 2 |                               |
| Reagent for hydrogen sulfide and mercaptans stripping Reaton-21-2 | LLC Reaton, Kazan             |
| Specifications 2458-014-94296805-2008, changes N 1 Hydrogen sulfide and mercaptan neutralizer Sulfanox | LLC Mirrico, Kazan            |
| Specifications 2458-067-94296805-2010 Hydrogen sulfide and mercaptan reagent-neutralizer INS-1, TY 2456-003-84449478-2009 Desoufion-SNPCH-1200 | LLC “NPP “Impuls”, Ufa       |
| Specifications 2458-006-66875473-2013 | “NIIneftepromchim” JSC       |

Table 2. Experimental data from laboratory studies on the content of mercaptans in the original oil at 545 ppm.

| Reagent                | The residual content of mercaptans, ppm |
|------------------------|----------------------------------------|
|                        | 1 h          | 2 h          | 4 h          | 24 h         |
| DARSAN (mark N)        | 320          | 280          | 260          | 250          |
| Reaton-21-2            | 200          | 120          | 100          | 50           |
| Sulfanox               | 260          | 240          | 200          | 150          |
| INS-1                  | 200          | 150          | 125          | 52           |
| Desoulfon-SNPCH-1200   | 140          | 100          | 60           | 40           |

Table 3. Experimental data on the refinement of the specific consumption of reagents with the content mercaptans in the original oil at 545 ppm.

| Reagent                | Specific consumption of reagent, kg/t | The residual content of mercaptans, ppm | Consumption ratio |
|------------------------|--------------------------------------|----------------------------------------|-------------------|
|                        |                                       | 4 h          | 24 h          | 4 h          | 24 h          |
| Reaton-21-2            | 1.13                                  | 184          | 84            | 3.1          | 2.4           |
| Desoulfon-SNPCH-1200   | 1.08                                  | 87           | 54            | 2.3          | 2.2           |
| INS-1                  | 1.4                                   | 220          | 142           | 3.9          | 3.5           |
The next stage of selecting a neutralization reagent was the reduction of the mass fraction of mercaptans in oil to 80 ppm and the determination of the actual consumption factor of the three most efficient samples. The results of the studies are presented in Table 3.

The results showed that the consumption ratios of the samples were of close value. However, it should be noted that when oil is water cut less than 10%, the reaction products of the interaction between the reagent-neutralizer and mercaptans precipitated, so in order to avoid the formation of sediment, 10% of freshwater was poured into the oil. Figures 2 and 3 present data of visual observations [26-28].

Results of laboratory research allowed us to choose the most optimal neutralizer, set its flow rate, and temperature of oil heating [29-30]. In addition, it influence of the place where the reagent - neutralizer is introduced into degassed oil is studied.

4. Conclusion
The studies stated that the most effective results on the residual content of mercaptans in purified oil are achieved by adding the reagent-neutralizer to degassed oil after the second stage of separation. Also, the tests proved that water in oil has an effect on the flow of reaction.

The action of the reagent-neutralizer takes place at the “oil-water” phase boundary, the dispersion contributes to the strengthening of mass interchange reducing the response time of the neutralizer with oil. The mode of supply of the reagent-neutralizer should be continuous as when the supply of the reagent is ceased, the process of neutralizing hydrogen sulfide discontinues.

The laboratory tests made it possible to select the best neutralizer Desoulfon-SNPCH-1200, to determine its minimum specific consumption and the temperature of heating oil. The application of this reagent-neutralizer will allow doing the effective oil preparation at the loading point of the Borodino field.

The amount of Desoulfon-SNPCH-1200 needed to neutralize the mercaptans depends on their content in oil and the required degree of reduction. The usual proportion in processing is 4-5 ppm of Desoulfon-SNPCH-1200 at 1 ppm of mercaptans.

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