

Environmentally friendly regeneration of used energy oils

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Abstract. The article covers the problem of regeneration of used petroleum oils, i.e., transformer, turbine and compressor oils in order to restore their physical and chemical properties and return them for their reuse for their intended purpose. In order to restore the petroleum oils purified from undesirable impurities, the Ionol antioxidant nozzle was implemented. The conducted studies have shown the possibility of using dehydrated Navbakhor bentonite and Kermine opoka-like clay for the regeneration of used oils. The regeneration of the waste compressor KP-8S used oil of Navoiyazot JSC was carried out under laboratory conditions using a local sorbent of opoka-like clays of the Kermine deposit. The resulting regenerated oils have a high and time-stable demulsifying ability and the rest of the inspected physical and chemical properties comply with the GOST standards.

1 Introduction

When using mainly easily accessible energy sources in economic circulation for a long period, the resource and technological base of the energy sector led to a large extent contributed to the emergence of environmental, social, scientific and technical problems in society, which are now affecting the life of mankind.

The way out of this situation is the rational and balanced consumption and protection of the entire complex of natural resources, aimed at increasing the social and economic potential, the quality of life of the population, the realization of the rights of present and future generations to use the natural resource potential and a favorable environment.

Waste lubricants belong to the life products of society and are characterized by unsatisfactory environmental properties, i.e., toxicity, carcinogenicity, fire and explosion hazard. Therefore, their environmentally safe disposal is necessary, which involves processing to obtain products that meet the requirements of consumers in terms of quality. At the same time, both the task of reducing the consumption of natural resources and the disposal of waste materials, as well as providing enterprises with inexpensive scarce oils, is being solved.

During long-term operation, petroleum oils change their physical, chemical and operational properties, "age". Oil aging occurs not only due to the oxidation of its

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hydrocarbons by atmospheric oxygen under the influence of elevated temperature and in the presence of metals, but also under the influence of flooding, salts, oxidation of the metals of the containers in which they are located, contamination with mechanical impurities, etc.

As a result of changes in the physical-chemical properties of the oil during oxidation, its performance properties usually deteriorate. Oils are drained or accumulated in huge quantities in warehouses. Regeneration in order to return them for further use or recycling in order to obtain the products necessary for the needs of various sectors of the economy is the most urgent task of today.

It is known [1] that the following petroleum oils are distinguished: regenerated - these are oils that have been processed according to one of the regeneration methods, reduced - regenerated oil stabilized by an additive, operational - poured into the equipment and in operation, the performance of which corresponds to the established standards for operational oil from the moment putting into operation until the moment of draining for regeneration. Used oil - to be drained or drained from the equipment due to non-compliance with the standards for the quality of operating oil in one or more indicators.

The problem of regeneration of used petroleum oils - transformer and turbine oils in order to restore their physical and chemical properties and return them for their reuse for their intended purpose is considered in this article.

According to the classification of Beloselsky S.P. these oils are classified as energy oils [2], because used in power equipment.

2 Materials and methods of research

There are various methods for the regeneration of petroleum oils: physical, chemical and physical-chemical methods. As the most effective method, we chose the method of adsorption purification. The high purification effect and the simplicity of the process are the main advantages of this method [3].

The use of local cheap and available natural mineral adsorbents with a sufficiently high adsorption capacity is of great national economic importance. Bentonite (alkaline) from the Navbakhor deposit, which was discovered in 1998, was used as an adsorbent for the regeneration of transformer and turbine oils. The material composition of these bentonite clays has been studied and reported in [4,5] with the involvement of complex laboratory methods (chemical, thermal, ESDO electron microscopic and X-ray diffraction analyses).

The capacity of Navbakhor bentonite for a number of oil components under dynamic conditions has been determined by adsorption-cryoscopy analysis [6].

It has been established that Navbakhor bentonite thermally activated up to 250°C can be used to purify petroleum oils.

The first stage of regeneration of used oils was their sedimentation from various mechanical impurities and water. It is based on the settling of particles in a liquid in suspension. Under the action of gravity, water and mechanical impurities, which have a higher density than oil, settle when standing still. Under laboratory conditions, they were settled in separating funnels with a volume of 1 liter during the day. At the same time, three layers were formed - a dense sediment at the bottom, an aqueous layer above it, and an oil layer at the top. The two lower layers were removed [7]. It should be noted that the water layer of the turbine oil turned out to be larger than that of the transformer oil, which can be explained by the operating conditions of the oil.

The objects of study were waste oils: transformer oil (sample from the railway depot) and turbine oil (sample from thermal power plant). It should be noted that these initial oils, the industrial production of which is organized at the Fergana Oil Refinery, are high-quality oils [8]. However, during long-term operation, like all oils, they "age".

3 Results and discussions

The research results are shown in Table 1.

Table 1. The results of the process of settling from various mechanical impurities and water.

| Used oils | Sediment (% mass) | Water (% mass) |
|-------------|-------------------|----------------|
| Transformer | 0.01 | 0.10 |
| Turbine | 0.10 | 10.00 |

Additional drying of waste oils from moisture was carried out by introducing synthetic zeolite CaA calcined at 500 °C. This particular zeolite was used, because it is brought to the Republic for natural gas dehydration.

In order to restore the petroleum oils purified from undesirable impurities, the Ionol antioxidant nozzle was introduced. Based on the literature data [9], we chose the Ionol concentration of 1% when introduced into oils. The oxidation of petroleum oil hydrocarbons with Ionol is inhibited by the following mechanism (Figure 1). At the first stage, Ionol reacts with peroxide radicals of oxidized hydrocarbons to form a stable phenoxyl radical, which is unable to continue the chain of hydrocarbon oxidation:

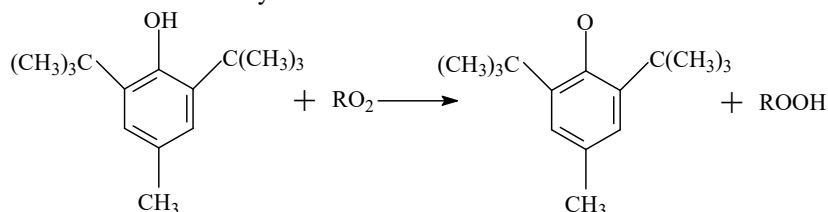


Fig. 1. Oxidation of petroleum oil hydrocarbons by ionol.

The adsorbent was crushed to a fraction of 0.5-1.0 mm, then dried in drying chamber at a temperature of 180-200 °C for 6 hours. The oil was purified under laboratory conditions, at room temperature, by percolation filtration in a glass column 1 m high, 4.5 cm wide. Sorbent taken 30% of the weight of the oil. After the adsorbent was introduced into the column, the oil was poured to the top of the column and kept closed for 4 hours, then it was filtered by gravity at a rate of 1 drop per 5 seconds and passed into the receiver until it completely drained. The selection of fractions was controlled by the refractive index. Three fractions were selected: I, II, III with different refractive indices. Then, the nonpolar solvent cyclohexane (the adsorption index of which is 3.3) was poured into the column, and the oil remaining on the sorbent was extracted. Cyclohexane is distilled off, and the residue is brought to constant weight. This is the IV-fraction. It had an indicator of waste oil.

Below are the results of the regeneration of used oils by Navbakhor bentonite in one adsorption - desorption cycle:

Table 2. Results of regeneration of used oil.

| No. of fraction | Oil yield, in mass % | |
|-----------------|----------------------|---------|
| | Transformer | Turbine |
| I | 12.50 | 13.00 |
| II | 18.50 | 14.90 |
| III | 26.60 | 30.00 |
| IV | 36.80 | 42.10 |

The physical-chemical parameters and the group chemical composition for the separated fractions of oils were determined by the adsorption-cryoscopy method [10]. As an example, we present the results of such measurements for transformer oil (Table 3).

Table 3. Physical-chemical parameters of selected fractions of transformer oil.

| No. of fractions | Refractive index | Density at 20 C, kg/m ³ | Kinematic viscosity, ν, cSt |
|------------------|------------------|---------------------------------------|--------------------------------|
| I | 1.4844 | 0.8311 | 24.80 |
| II | 1.4856 | 0.8400 | 22.90 |
| III | 1.4877 | 0.8550 | 19.10 |
| IV | 1.4868 | 0.8608 | 16.23 |

The group composition is as follows (mass %): aromatic - 18.18; n-paraffin - 13.63; iso-paraffin + naphthenic hydrocarbons - 28.19.

In order to regenerate the adsorbent using various desorbents from the eluotropic series, the desorption of adsorbed substances from bentonite was carried out and it was shown using IR and GLC that they represent about 90% of physically adsorbed oxygen-containing substances and 10% of their salts.

In the Republic of Uzbekistan, there is a huge raw material base of natural sorbents - bentonite clays, flasks and opoka-like rocks - the value of which is determined by high activity and good adsorption properties.

We also carried out the regeneration of the waste compressor KP-8S waste of Navoiyazot JSC in the laboratory conditions of the Institute of General Organic Chemistry of the Academy of Sciences of the Republic of Uzbekistan with the help of a local sorbent of opoka-like clays of the Kermine deposit located in the Navoi region.

At present and earlier in many countries of the world, including the United States, Russia and others, work on improving the technology of used oil regeneration has been and is being carried out. One of the main and classic methods of purification of used oil is adsorption purification. However, this method uses expensive, imported both synthetic and natural types of adsorbents (zeolites, silica gels, bentonites, clays, etc.). Another method is vacuum distillation. But, in this case, the process is carried out with the involvement of special expensive equipment and a large expenditure of energy resources.

In our study, it is proposed to clean and regenerate oils from unwanted products of oil oxidation using local types of adsorbents.

Up to 56 tons of used compressor oil KP-8S is annually accumulated at Navoiyazot JSC. The objective of this study is to study the possibility of cleaning existing used oils with their return to the production cycle. At the same time, a number of pressing issues related to both the disposal of used oils, which represent an environmental problem, and the reproduction of lubricants from recycled waste resources are solved.

The waste oil processing technology provides for the acceptance of raw materials, its evaluation, and the determination of physical and chemical characteristics. Processing stages include dehydration, purification from mechanical impurities, adsorption purification and other types of mechanical and chemical processing. Bringing the physical-chemical characteristics of refined oil to the standards of GOST.

KP-8S oil was studied under laboratory conditions for its purification and regeneration by several physical-chemical methods [10].

The chemical composition of Kermine opoka-like clays was studied, it was found that the content of active silicic acid and the activity of CaO differ from ordinary opoka. Thus, the content of SiO₂ in the studied rocks is significantly lower than in others, and is, as it were, inversely related to the amount of CaO and CO₂. But the studied clays are characterized by a high content of alumina (6.58-9.16%). This indicates the presence of a constant amount of clay minerals, apparently, of the montmorillonite group, in the Kermine opoka-like rocks. The studied rocks also differ in that they contain 18% CaO and up to 2% SO₃. The relatively high content of SO₃ is explained by the presence of gypsum and sodium sulfate in the rock.

The activity of Kermine opoka-like clays is directly dependent on the content of active silicic acid.

According to the data of chemical analyzes of <0.001 mm fractions, the content of the main components in all varieties of rocks is quite close. The content of Al_2O_3 in opoka-like clay rocks, underlying and covering clays, ranges from 14.58 to 18.18%. This is obviously associated with the removal of Al_2O_3 as a result of the formation of zeolite.

Iron is part of the crystal lattice of clay minerals, as evidenced by both the greenish-gray color of the rocks and the absence of iron hydroxides (limonite) in them. The incorporation of Fe_2O_3 into the crystal lattice is obviously associated with the simultaneous removal of Al_2O_3 during rock zeolitization.

Determination of the chemical composition (mass%) showed that the main clay mineral of the Kermine deposit is montmorillonite.

One of the ways to activate Kermine opoka-like clays is heat treatment. Thermal treatment of natural sorbents affects their adsorption activity. It was determined that with an increase in the activation temperature, the activity increases to a maximum and falls due to dehydration of the samples. Clay (fineness 150-20 microns) was thermally processed by us at 150-200 °C with exposure to constant weight.

Waste oils were purified under laboratory conditions in one adsorption cycle at room temperature in a glass column 1 m high and 4.5 cm wide. Sorbent taken 40% of the weight of the oil. After the adsorbent was introduced into the column, the oil was poured into the top of the column and kept closed for 4 hours, then it was filtered by gravity at a rate of 1 drop per 5 sec. (this is about one volume per hour) was passed into the receiver until it was completely empty. A sample was taken and the comparative physical-chemical parameters of the purified oil with the used oil were determined. The results of the study are shown in Table 4.

Table 4. Comparative basic physical and chemical parameters of used and purified KP-8S compressor oil.

| No. | Name of indicators | Commodity oil | Source oil | Used oil | Purified used oil |
|-----|---|--|------------|----------|-------------------|
| 1 | Kinematic viscosity, at 40 °C, mm^2/s | 41.4-55.0 | 34.76 | - | 34.32 |
| 2 | Density at 20 °C, kg/m^3 | Not standardized, definition is obligatory | 0.873 | - | 0.874 |
| 3 | Flash point, closed crucible, °C, not lower | 205 | 190 | - | 192 |
| 4 | Acid number, mg KOH per 1 g of oil, not more | 0.05 | 0.05 | 0.04 | 0.03 |
| 5 | The content of mechanical impurities | Absence | Absence | Absence | Absence |
| 6 | Water content | Absence | Absence | Absence | Absence |

Results of Table 4 show that, according to the main physical and chemical indicators, KP-8S purified used oil meets the regulatory requirements and fully complies with the GOST standards.

A material balance was drawn up, the yield of purified waste oil KP-8S was 76%.

4 Conclusion

The conducted studies have shown the possibility of using dehydrated Navbakhor bentonite for the regeneration of used oils: about 15% of oils are purified in a one-time adsorption-desorption cycle.

The optimal conditions for the regeneration of energy oils have been established: the ratio of S:L, the size of the sorbent grains, its activation, solvents, desorbents, temperature, etc. The main parameters of the processes of adsorption-desorption of oils have been worked out, which form the basis of the concept of their regeneration.

Conducted comprehensive studies of the obtained oils have shown that they have a high and time-stable demulsifying ability and the rest of the inspected physical and chemical properties comply with the GOST standards. The absence of moisture in used and regenerated samples of transformer and turbine oils was controlled by the Dean and Stark method.

The main technological parameters of the adsorption purification process have been worked out on an enlarged laboratory installation, and prototypes have been developed. Based on the data obtained, the relevant regulatory and technical documentation was developed.

The polyminerality of opoka-like rocks of Kermine was determined; montmorillonite is the main rock-forming clay mineral, hydroxide is present in a smaller amount, magnesian silicates and kaolinite are noted as an impurity.

It has been proven that Kermine opoka-like clays have sufficient cleaning and bleaching properties in relation to mineral used compressor oils.

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