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APPLICATION OF VACUUM DISTILLATION FOR THE USED MINERAL OILS RECYCLING

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Abstract. The physico-chemical properties and the group composition of the used mineral motor oils M-10DM and NORMAL 15W40, as well as the fractions obtained as a result of their vacuum distillation, have been studied. The results of IR spectroscopy and XRF analysis are presented. The change in the composition and properties of the fractions distilled from used oils under vacuum has been described.

Keywords: vacuum distillation, used oil, IR spectroscopy, oil recycling.

1. Introduction

Nowadays, the majority of lubricants, the consumption of which grows with each passing year, is imported into Ukraine, making it dependent on foreign countries. The solution of this problem is to improve the methods of used motor oils recycling. On the one hand new methods allow to cut the costs for expensive lubricants significantly, on the other hand, we solve the problem of oils utilization and prevent environment pollution.

In Ukraine the used motor oils (UMO) are mainly burned, which is irrational both from the economic and environmental standpoints. It is more efficiently to direct UMO for recycling to obtain components of base oils or lubricants of different purposes [1-3]. Utilization of UMO is an important scientific and technical problem, because these industrial wastes negatively affect the environment. Pollution of water by used oils makes up 20 % of the total technogenic pollution or 60 % of the pollution by petroleum products. The conseguences of UMO disposal and burning sometimes create even more complex environmental problems than UMO themselves, representing a significant threat to the biosphere [4, 5].

UMO recycling is carried out through the joint use of physical (settling, filtration, centrifugal purification, evaporation and vacuum distillation), chemical (sulfuric acid refining, hydrofining) and physico-chemical (coagulation, adsorption) methods.

In the United States UMO is refined using the Aguanetics Inc. system, where fine filtration in combination with a low-temperature vacuum is used. The "BoothOilCo" company implements the UMO recycling in a thin-film evaporator according to the scheme: separation of solids on a mesh filter, evaporation of water, vacuum distillation of low-boiling components, high vacuum film evaporation of oil fractions, adsorption, contacting and filtration. The Ecoil recycling unit uses a VPH Thor cleaning system, consisting of a vacuum unit, heater, degasser, several separators/coagulators for macro-particles and water removal. The Mohawk Lubricants process, developed in Canada, involves single evaporation of raw materials, vacuum distillation, two-stage distillation in thin-film evaporators and hydrofining with subsequent treatment of oil by sodium hydroxide [6-9].

When analyzing the known processes of UMO recycling, we can say that vacuum distillation is an integral part of any processes. Rotary-film vacuum units are used as the main apparatus abroad, and vacuum columns – in the domestic processes.

Previously [10, 11] we studied the change in the operational properties and the group hydrocarbon composition of UMO, confirmed the formation of oxygen-containing products of oils "aging" during their long-run use in the combustion engines, and explained the change in the composition of the inorganic part of motor oils provided by the action of spent additives and falling of the engine wear parts into the oil products. The results obtained can serve as the source information for choosing the optimal recycling technology.

A. Grigorov [12] determined that viscosity, density and purity of UMO were changed due to vacuum distillation. However, in our opinion, the results obtained are not sufficient to assert that the produced oil distillate can serve as a base component of oils or be used independently as a lubricant.

The purpose of this work is to study the properties of used mineral motor oils M-10DM, NORMAL 15W40 and the fractions obtained as a result of their vacuum distillation to determine the possibilities of their further use.

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2. Experimental

Used mineral motor oils M-10DM and NORMAL 15W40, removed from crankcases of diesel and gasoline engines, respectively, after the end of their service life were the starting materials for researches.

The oils were distilled at 623 K and residual pressure of 1.07–1.20 kPa, and the following fractions were obtained: strippant, oil fraction and residue. The products were studied and analyzed according to standard methods described below.

The density was determined using a picnometric method; viscosity – by viscosimetry, flash point – using the open type device [13]. The group composition was studied by a liquid chromatography. The silica-alumina gel of ASK type was used as an adsorbent. Fractions of hydrocarbons were washed out by petroleum ether and benzene, and asphalt-resinous substances were desorbed by alcohol-benzene mixture.

XRF analysis was carried out to determine the elemental composition of the oil using a mobile precision analyzer EXPERT 3L. For the analysis we prepared oil samples, which were burned at 723 K for 4 h, cooled in a desiccator and then the obtained films were grinded [14].

IR spectroscopy was performed on Spectrum Two FT-IR spectrometer (Perkin-Elmer); the cell was made of zinc selenide with 0.1036 mm of thickness. The program Spectrum v.10.03.06 was used for the analysis.

3. Results and Discussion

3.1. Physico-Chemical Properties

As a result of vacuum distillation, there is a change in the physico-chemical characteristics of the studied UMO. The operational characteristics of resulting strippant, oil fraction and residue are represented in Tables 1 and 2.

One can see from the tables that the operational properties of strippant and oil fraction are similar. They are characterized by lower values of acid number and total base number compared with UMO, low ash content and the content of mechanical impurities. The strippant has a slightly higher water content, while in the oil fraction there are only its traces. The oil fraction has a lower viscosity compared with the used oil. At the same time, the residue after vacuum distillation is characterized by high values of ash content, coking capacity, content of mechanical impurities and acid number.

Additives added to mineral motor oils, in order to improve their operational properties, have an acid-alkaline basis. Thus, during the production of commercial oils, when an additive is added to the base oil with a low acid number, there is an increase in the total base number and a slight increase in acidity (no more than 0.8–1.2 mgKOH/g). The increase in base number increases the ability of motor oils to neutralize corrosive and aggressive

Table 1

Characteristics of fractions obtained after vacuum distillation of M-10DM used oil

Index	M-10DM used oil	Fractions of used oil		
		Strippant	Oil fraction	Residue
Viscosity, mm^2/s:				
υ_{50}	51.65	17.90	61.27	118.54
υ_{100}	10.22	4.61	10.88	16.42
$\upsilon_{50}/\upsilon_{100}$	5.05	3.88	5.63	7.22
Viscosity index	88	100	90	76
Density, kg/m^3	884	855	864	914
Acid number, mgKOH/g	2.71	2.63	1.54	2.30
Total base number, mgKOH/g	0.35	0.34	0.29	0.25
Water content, %	0.14	1.02	traces	traces
Content of mechanical impurities, %	0.062	traces	0.019	0.231
Coking capacity, %	2.30	0.19	1.55	7.04
Ash content, %	0.940	0.001	0.015	4.620
Freezing point, K	254	250	255	259
Flash point, K	488	467	511	547
Fraction yield, wt %	–	10.05	67.92	22.03

Table 2

Characteristics of fractions obtained after vacuum distillation of NORMAL 15W40 used oil

Index	NORMAL 15W40 used oil	Fractions of used oil		
		Strippant	Oil fraction	Residue
Viscosity, mm^2/s:				
υ_{50}	69.81	36.42	64.19	76.30
υ_{100}	13.96	8.17	11.87	12.29
$\upsilon_{50}/\upsilon_{100}$	5.0	4.46	5.41	6.21
Viscosity index	110	114	98	82
Density, kg/m^3	896	864	889	923
Acid number, mgKOH/g	1.96	1.87	1.05	1.35
Total base number, mgKOH/g	3.46	3.06	2.85	2.09
Water content, %	0.15	1.21	traces	traces
Content of mechanical impurities, %	0.039	traces	0.007	0.173
Coking capacity, %	1.71	0.08	1.16	6.94
Ash content, %	0.534	0.002	0.023	1.64
Freezing point, K	255	248	250	257
Flash point, K	511	460	515	540
Fraction yield, wt %	–	10.52	67.09	22.39

acidic products that are formed during its oxidation. At first the acid number decreases owing to additives depletion during the operation, but then it increases due to the accumulation of acidic compounds in the oil. The substances which are formed due to the additives thermal decomposition in some cases cause corrosion of engine parts, and in some cases inhibit the oxidation processes.

To our mind, the change in the acid number of fractions obtained after vacuum distillation can be explained by the proceeding of decarboxylation reactions accompanied by CO_2 removal from the carboxyl group of naphthenic acids or their derivatives while heating and the presence of metal particles, which are formed due to engine parts wear and exhibit catalytic action, according to the following reaction:

$$R-COOH \xrightarrow{t} CO_2 \uparrow + RH$$

During vacuum distillation, under the influence of temperature and residual pressure, the evaporation of volatile carboxylic acids boiling in the range of 523–563 K and the decarboxylation of naphthenic acids at 537–673 K occur. As a result, the resulting strippant is characterized by the acid number, the value of which is higher than that of the oil fraction.

3.2. Group Hydrocarbon Composition

The results of group composition analysis (Fig. 1) confirmed the following distribution of the hydrocarbon fraction in the used oil:

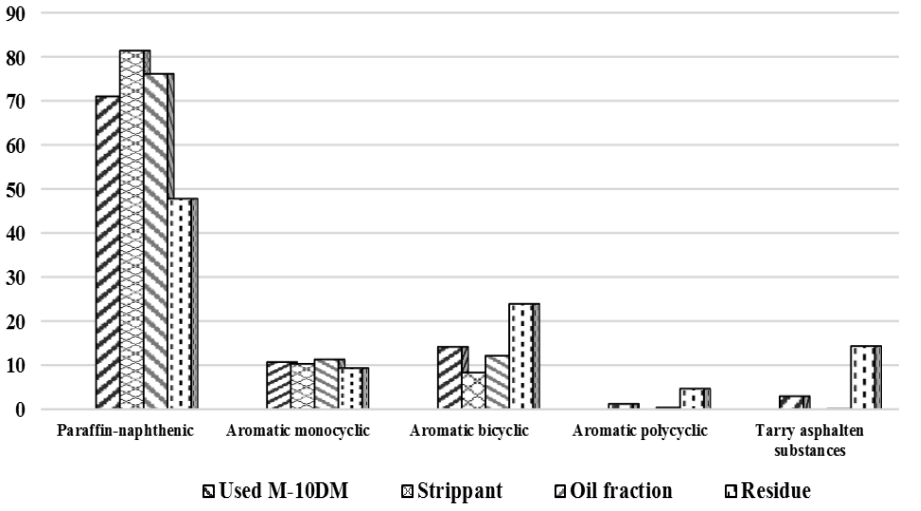
- strippant is characterized by a higher content of paraffin-naphthenic hydrocarbons compared to the used oil, small amount of mono- and bicyclic aromatic hydrocarbons and the absence of polycyclic aromatic hydrocarbons and asphalt-resinous substances;
- oil fraction has paraffin-naphthenic hydrocarbons and small amount of mono- and bicyclic aromatic hydrocarbons;
- residue is characterized by a significant amount of mono-, bi- and polycyclic aromatic hydrocarbons and asphaltic-resinous substances.

The base oils containing 65–75 % of paraffin-naphthenic hydrocarbons and 35–25 % of aromatic hydrocarbons, including approximately 15 % of aromatic polycyclic ones have the best properties. The increase or decrease in the amount of paraffin-naphthenic hydrocarbons in oils and corresponding lower or higher content of aromatic hydrocarbons worsen their performance.

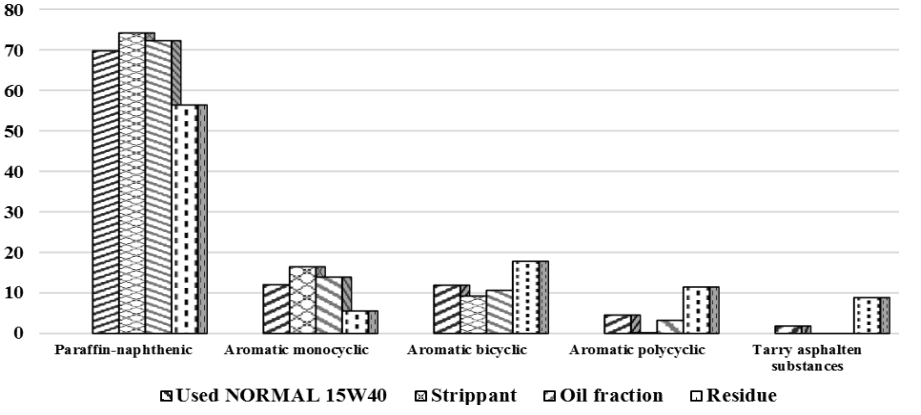
3.3. X-Ray Fluorescence Analysis

The strippant and the oil fraction have low ash content and coking capacity (Table 1, 2). At the same time, these values for the residue were much higher. Therefore, it was important to determine the inorganic composition of the residues. The investigation results are given in Tables 3 and 4.

So, the residues after vacuum distillation contain the elements that were both in the additive and in the parts of the engine. Their presence in M-10DM and NORMAL 15W40 was established earlier [10, 11]. Excessive content of these metals indicates that after vacuum distillation, under the influence of temperature, thermal decomposition of additives occurs. Moreover, the accumulation of high-boiling components (asphalt-resinous substances, *etc*.) is confirmed by the previously determined group hydrocarbon composition. Low values of acid and total base numbers indicate the change in the amount of additives.



a)



b)

Fig. 1. Group hydrocarbon composition of the fractions after M 10DM (a) and NORMAL 15W40 (b) vacuum distillation

Table 3

XRF of the residues after M-10DM vacuum distillation

Element	Content, ppm	
	in M-10DM used oil	in residue after vacuum distillation
P	2950.99	13279.46
S	6166.21	27747.95
Ca	16006.38	72028.71
Ti	53.79	242.06
Mn	7.09	31.91
Fe	307.10	1381.95
Zn	4033.07	18148.82
Sr	4.14	18.63
Zr	0.17	0.77
Mo	1.48	6.66
Pb	26.90	121.05

Table 4

XRF of the residues after NORMAL 15W40 vacuum distillation

Element	Content, ppm	
	in M-10DM used oil	in residue after vacuum distillation
Mg	549.75	2474
Si	139.97	630
P	2797.05	12587
S	6401.21	28805
Ca	1445.68	6506
Cr	52.63	237
Mn	8.8	40
Fe	696.36	3134
Ni	5.81	26
Cu	74.05	333
Zn	4360.95	19624
As	2.99	13
Rb	1.99	9
Sr	2.16	10
Mo	48.15	217
Pb	16.11	72

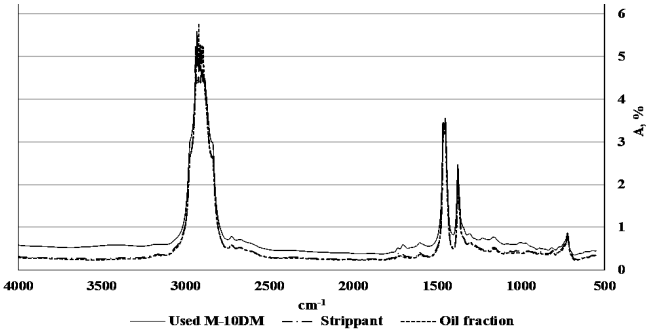
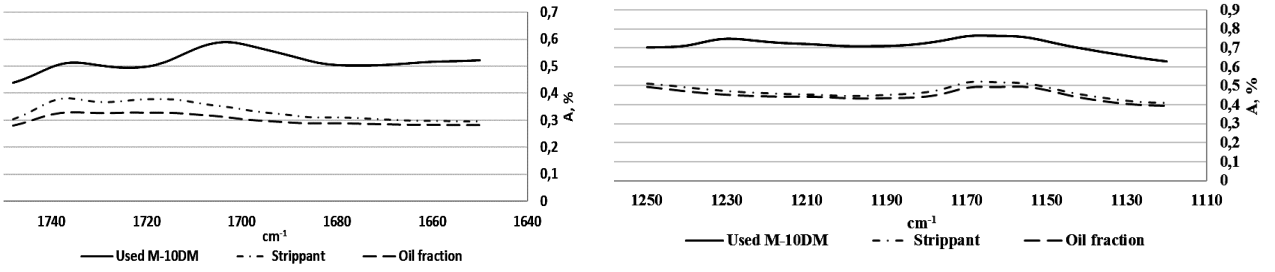


Fig. 2. IR spectra of M-10DM used oil and its fractions after vacuum distillation



a) b)

Fig. 3. Change in adsorption bands intensity of carboxylic acids (a) and their derivatives (b) after vacuum distillation of M-10DM used oil

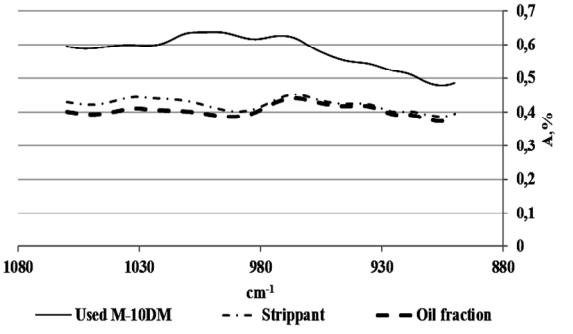


Fig. 4. Change in adsorption bands intensity of antiwear additive after vacuum distillation of M-10DM used oil

3.4. IR Spectroscopy

IR spectroscopy was used to confirm the structural group composition of UMO and the fractions obtained after vacuum distillation. The results are shown in Figs. 2-4.

As can be seen from Fig. 2, IR-spectra of the strippant and oil fraction differ from the spectrum of the initial M-10DM. Paraffin-naphthenic hydrocarbons in the spectra of the resulting fractions were identified by stretching vibrations at 2935–2915 cm^{-1}, as well as deformation vibrations of CH group at 1470–1445 cm^{-1} and stretching vibrations of C–C group at 1740–1720 cm^{-1}. The presence of aromatic hydrocarbons was confirmed by an intensive absorption band of deformation vibrations of CH group at 860 cm^{-1}. In addition, the skeletal vibrations of C–C bond of the aromatic nucleus were detected by absorption bands in the region of 1610–1600 cm^{-1}.

In the used oil we also observe alcohols, aldehydes, ketones, organic acids, *etc*., which are the products of of oil aging. Their presence is confirmed by the absorption bands of C=O stretching vibration at 1740–1690, 1820–1740 cm^{-1} and asymmetric stretching vibrations of C–O bond at 1260–1150 cm^{-1} (Fig. 3), which is confirmed by changing the absorption bands of organic acid derivatives.

Previously [8] we established the presence of anti-wear additive ZDDP in the used oil, which was confirmed by absorption bands at 1020–960 cm^{-1}. The intensity of similar bands for the fractions after vacuum distillation of M-10DM is less, indicating a decrease in amount of additives. This is in agreement with the previously conducted XRF analysis of the resulting fractions and the absence of metal elements in them. The change in the intensity of the additive absorption bands is presented in Fig. 4.

The IR spectra of the used oil NORMAL 15W40 and the fractions after its vacuum distillation have a similar dependence, and their spectra are shown in Fig. 5. There are minor changes in the group composition of the samples, as well as a decrease in the intensity of absorption bands of oxygen-containing aging products in the initial oils, indicating a reduction of their amount in the fractions after vacuum distillation.

Stretching vibrations of C=O bond point the presence of carboxylic acids, which is confirmed by absorption bands at 1740–1690 cm^{-1}, as well as stretching vibrations at 1820–1740 cm^{-1} and asymmetric stretching vibrations of C–O bond in the region of 1260–1150 cm^{-1}, indicating a change in the absorption bands of carboxylic acids derivatives.

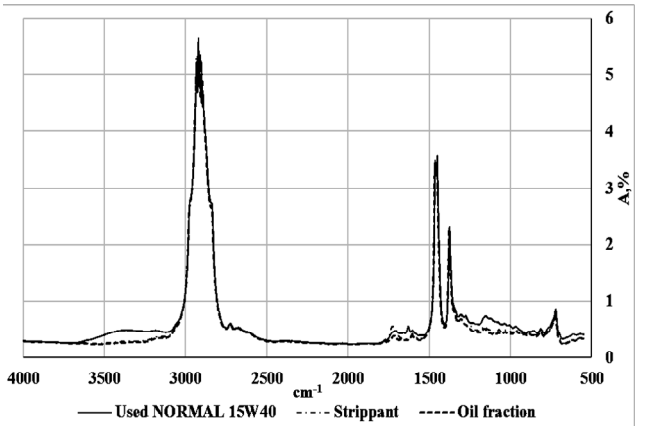


Fig. 5. IR spectra of NORMAL 15W40 used oil and its fractions after vacuum distillation

4. Conclusions

The operational properties and the group composition of M-10DM and NORMAL 15W40 used oils, as well as the fractions obtained after their vacuum distillation have been studied. The change of the hydrocarbon fraction distribution in the resulting fractions has been established. The hydrocarbon composition and change in the amount of oxygen-containing products of the obtained fractions in comparison with the used oil were confirmed by IR spectroscopy. By means of XRF analysis it was established that due to the vacuum distillation of used oils, the metals of the additive are concentrated in the residue. We can state that since vacuum distillation of UMO does not provide sufficient purification degree of used oils and additional purification methods are needed, then vacuum distillation may be an integral part of the combined industrial process of used oils regeneration.

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ЗАСТОСУВАННЯ ВАКУУМНОГО РОЗДІЛЕННЯ В ТЕХНОЛОГІЇ РЕГЕНЕРАЦІЇ ВІДПРАЦЬОВАНИХ МІНЕРАЛЬНИХ ОЛИВ

Анотація. *Вивчено фізико-хімічні властивості та груповий склад відпрацьованих мінеральних моторних олив М-10ДМ та NORMAL 15W40, а також фракцій, одержаних в результаті їх вакуумного розділення. Наведено результати ІЧ-спектроскопічного та рентгенофлуоресцентного аналізу відпрацьованих олив та виділених фракцій. Описано зміну складу й властивостей фракцій виділених з відпрацьованих олив внаслідок їх вакуумного розділення.*

Ключові слова: *вакуумне розділення, відпрацьована олива, ІЧ-спектроскопія, регенерація олив.*