

ECOLOGY OF USED ENGINE OIL ADDINOL

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Abstract

Comprehensive spectroscopic studies of used and regenerated with chloric acid samples of ADDINOL engine oil were carried out. It was revealed that during the operation of engine oil, structural changes in hydrocarbon components, the formation of oxygen-containing compounds, and the accumulation of products of thermal destruction and friction occur. An assessment was made of the qualitative changes in used motor oil under the influence of chloric acid. Restoration of the structure of basic hydrocarbon components was established, complete removal of succinimide additives while retaining detergent-dispersant and extreme pressure additives, as well as removal of compounds containing hydroxyl groups and a highly dispersed carbon phase. It has been established that the precipitate is a carbon-containing agglomerate, which contains components of succinimide additives.

Keywords: used engine oil, chloric acid, carbon-containing agglomerate, IR spectroscopic, morphology, succinimide additives

I. Introduction

As is known, the determination of the chemical composition of the aging products of lubricating motor oils (mechanical impurities, additives, heavy metals, solvents, fuels, acids, oxidation, polymerization, degradation products, water, etc.) is the main task in studying the possibilities of their regeneration – recycling. The effectiveness of the recycling method used should also be confirmed by the results of a comprehensive analysis of regeneration products [1–3]. This problem can be solved only if several analytical methods are used simultaneously.

In this paper, based on the results of a comparative study of the spectroscopic features of the original, spent and subjected to acid regeneration with chloric acid, engine oil ADDINOL Super Light 0546, SAE 5W-40, the sources of contamination of the lubricant and the effectiveness of the re-generation are discussed.

II. Methods

Processed synthetic engine oil ADDINOL Super Light 0546, SAE 5W-40 was chosen as the object of research. The duration of its operation was 5 thousand km.

The method of regeneration of used oil ADDINOL Super Light 0546, SAE 5W-40 consisted of treatment with chloric acid and described in detail in [4,5]. The infrared spectra of motor oil were recorded on a Nicolet IS 10 spectrometers («Thermo Scientific») in the wavenumber range from 400 to 4000 cm⁻¹. The registered samples in the form of a drop were compressed between two

transparent silicon windows until a thin film (capillary layer) was formed.

The surface morphology, as well as the elemental composition of the solid deposit sample, were studied by transmission electron microscopy (TEM) on a JEM-2100 microscope with a grating resolution of 0.14 nm (with a built-in EDX analyzer (EDS, Genesis 4000, using a Si (Li) detector).) at an accelerating voltage of 100 kV. The TEM sample was fixated on carbon substrates mounted on copper grids.

III. Results

Lubricating oils are known to be multicomponent dispersed systems. In [4], based on the results of a comprehensive study of the physicochemical parameters and dielectric characteristics of used engine oil (UMO) ADDINOL Super Light 0540, SAE 5W-40, it was found that the main products of "aging" are fine soot particles. It was also found that UEO retains surfactant additives in its composition, the molecules of which envelop finely dispersed solid particles, preventing their coagulation and sedimentation even during prolonged settling (40 hours at temperatures up to 80°C), centrifugation and vacuum filtration. Efficient settling of fine particles became possible due to the ease of interaction between the used chloric acid, which is one of the strongest oxidizing agents, and the components that make up engine oil additives [5]. The resulting breakage of chemical bonds leads to degradation and loss of the functional properties of the additives, which leads to the ease of sedimentation of oil contaminants.

To confirm or refute this mechanism, studies were carried out on 4 samples of ADDINOL Super Light 0546 engine oil: sample 1 - original engine oil (before operation), sample 2 - used engine oil (after operation), sample 3 - regenerated engine oil, sample 4 - solid residue obtained during oil regeneration.

Let's consider some spectral features of the original, used, regenerated oil (Fig. 1; a, b and c, respectively). The spectra show that the nature of the oils is similar, but there are also fundamental differences. IR spectroscopic data of sample 1 (Fig. 1, a) suggest that the original motor oil has a complex composition and includes aliphatic hydrocarbons with long chain branching, polyorganosiloxanes, and esters of dicarboxylic acids. So, based on the data obtained, it can be argued that the basis of motor oil is polyolefins. There are two characteristic bands at 2853.03 and 2923.17 cm^{-1} , corresponding to the antisymmetric and symmetric stretching vibrations of C-H of the CH₂ group. In addition, the intensity of these bands, which makes it easy to identify them, indicates that these compounds have a polar group at the end of the chain. Scissor vibrations of the CH₂ group were noted for the medium strength band at 1459.37 cm^{-1} . An absorption band was also found at 966.76 cm^{-1} related to out-of-plane bending vibrations of hydrogen atoms bonded to carbon in the trans position in unsaturated olefin derivatives (disubstituted ethylene).

The presence of polyorganosiloxanes was also noted in the composition of the original motor oil: intense bands in the region of 100-1100 cm^{-1} indicate the presence of Si-O, out-of-plane deformation vibrations of unsymmetrical disabled ethylene at 889.35 cm^{-1} can correspond to both $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$ and $\text{R}^1\text{R}^2\text{C}=\text{CHR}^3$, however, the weak intensity of this band indicates the second type, since it is known that when the double bond moves from the end of the chain to the center of the molecule (the bond is in the chain), the intensity of the band will decrease. In addition, the band 1736.59 cm^{-1} in the region 1800-1750 cm^{-1} in the case of vinyl compounds is an overtone of the frequency 890 cm^{-1} and is a valuable confirmation of the presence of an unsymmetrical ethylene bond.

Absorption in the range of 3400 and 3200 cm^{-1} refers to intermolecular hydrogen bonds -OH of macromolecular compounds. In this case, the appearance of an absorption band of the bound OH group at 3388.42 cm^{-1} refers to the concentrated solution with a polymer association dissolved in a non-polar solvent (probably water in oil).

The bound group –OH is marked on the basis of a wide band of low intensity in the region of 3300-2500 cm^{-1} overlapped in places by stretching vibrations of C–H. The interval 3388.42 -3714.69 cm^{-1} falls on the absorption of the unbound group –OH. Esters of dicarboxylic acids are presented in the range 1180-1080 cm^{-1} in which there are 4 bands of different intensity, one of which contains a doublet (1150 cm^{-1}). These bands indicate antisymmetric and symmetric stretching vibrations of the C-O-C-O-C group in saturated polyesters.

In the region of about 680-610 cm^{-1} , bands which attributed to sulfates were noted. Considering the absence of the second very strong bands around is 1130-1080 cm^{-1} , which in most cases accompany sulfates and their weak character, as well as the duplicity of the bands at 608.72, 664.43, 673.10 cm^{-1} , we can conclude that these are alkaline bisulfates metals. A group of bands in the frequency range 2280-2730 cm^{-1} to the absorption of PO^+ stretching vibrations. These components are the most common additive components.

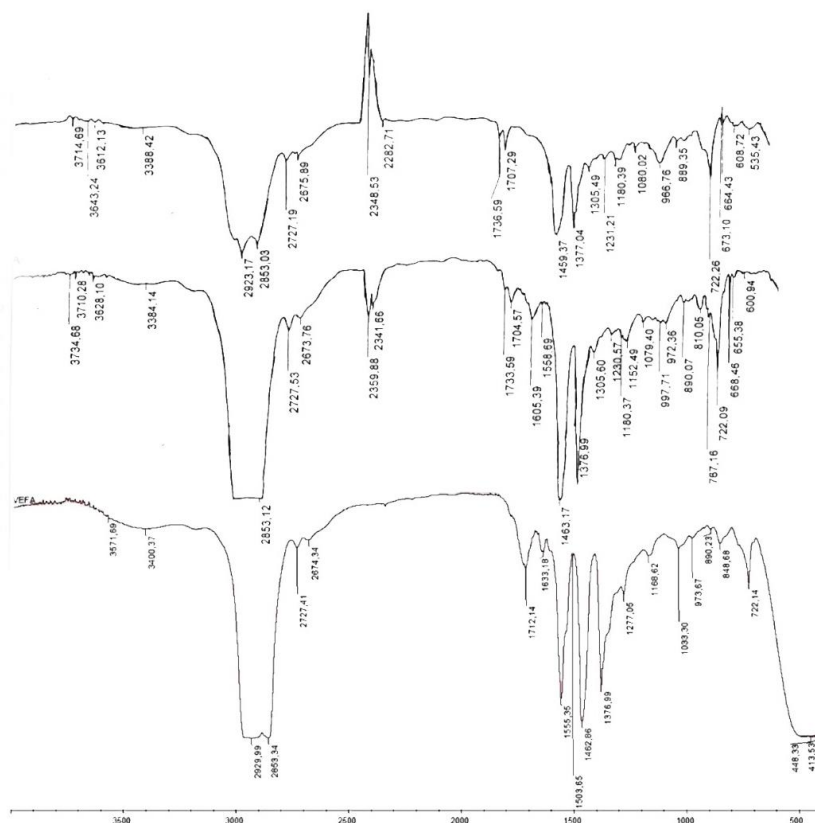


Fig. 1: IR spectra of engine oil ADDINOL Super Light 0546 (a - original; b - used; c - after regeneration)

On fig. 1, b shows the spectrum of sample 2 - engine oil after operation. An increase in the number of bands from 22 for the original motor oil to 28 for the used one makes it possible to judge the complication of the chemical composition of the used oil.

The structural changes that have taken place are especially clearly seen in the example of polyolefins: despite the fact that the general position of the absorption regions associated with the stretching and bending vibrations of the C–H bond of the CH_2 group is preserved, however, the absorption structure (number of bands, their intensity) changes. The region 2923-1450 cm^{-1} undergoes major changes, which is associated with deformation vibrations of α -olefin macromolecules, which consist of more complex monomeric units with lower symmetry. If the initial oil had absorption bands of medium strength (absorption intensity = $22 \div 26$), then in the used oil the absorption of these bands could be identified with difficulty (absorption intensity = $0.121 \div 0.828$), which may be caused by the removal of terminal polar groups that were noted in original.

It cannot be said that the absorption at 722 cm^{-1} , due to the pendulum vibrations of CH_2 groups, remained unchanged - a splitting of the band is noted (it is absent in the spectrum of the original oil), which is caused by significant changes occurring in the immediate environment of the oscillating groups. Such changes can include both external and internal influences (the appearance or absence of a hydrogen bond, mechanical and steric hindrances, the effects of inductive and dipole interactions, etc.). It can also be assumed that such a multilateral impact can be exerted by the previously discovered finely dispersed carbon particles of fuel combustion, which are formed during operation and are dispersed in the volume of used oil [4].

The occurrence of absorption bands of medium strength at 1558.69 cm^{-1} and weak at 1605.39 cm^{-1} corresponds to $\text{C}=\text{C}$ stretching vibrations conjugated with the neighboring oxygen atom or carbonyl group at the double bond. The formation of this type of compounds may be a consequence of oxidative processes accompanied by the formation of vinyl oxygen-containing compounds. This is confirmed by the appearance of a band at 997.71 cm^{-1} , which is related to outside planar bending vibrations of $\text{CH}=\text{CH}_2$ in vinyl compounds.

For heteroatom-containing compounds, it was noted that of the 2 bands assigned to bisulfates in sample 1, the 673.10 cm^{-1} band disappeared, and the 608.72 cm^{-1} band shifted to a lower frequency region up to 600.94 cm^{-1} and its characteristic doublet disappeared. In addition, a new medium-strength band appeared at 655.38 cm^{-1} . The absorption bands of phosphorus-containing stretching vibrations in the region of $2280\text{--}2730\text{ cm}^{-1}$ are shifted and less intense than in the spectrum of the original oil.

The study of the IR spectrum of sample 2 (Fig. 1, b) shows that the intensity of the absorption bands in the region of $3380\text{--}3735\text{ cm}^{-1}$, related to the stretching vibrations of the unbound OH group, remained practically unchanged, but there was a shift by $10\text{--}60\text{ cm}^{-1}$ of all bands without exception. According to the literature data, this effect is observed with an increase in the polarity of the solvent (accumulation of water and acid-type compounds).

Analyzing the IR spectrum of sample 3 - used oil subjected to acid cleaning with chloric acid (Fig. 1, c), one can see that the intense absorption peaks characteristic of bisulfates, phosphorus-containing compounds have completely disappeared (their disappearance indicates the occurrence of a chemical interaction between the components of succinimide additives and acid). But, along with this, there are also evidences of chlorine addition to the hydrocarbon chain - in the region of $750\text{--}800\text{ cm}^{-1}$, as well as two very weak new absorption bands of $\text{C}\text{--}\text{Cl}$ stretching vibrations at 413.53 and 448.33 cm^{-1} . This assumption is supported by the appearance of a new absorption band in the region of 1503.65 cm^{-1} , which is an overtone of the above bands.

But the most valuable result, in our opinion, is the nature of the band corresponding to pendulum oscillations $\text{--}(\text{CH}_2)_n\text{--}$: its splitting got disappeared and it has shifted to a higher frequency region. This result is in good agreement with the statement made above that it is the finely dispersed carbon particles of fuel combustion that are the factor responsible for the change in the oscillation frequency $\text{--}(\text{CH}_2)_n\text{--}$, and data on the high degree of coagulation of fine soot particles during regeneration.

And no less important is the disappearance of the bands related to the stretching vibrations of the OH group (after regeneration, the oil does not contain traces of polar hydroxyl groups) and the appearance of one of the most intense bands at 1555 cm^{-1} , which is probably associated with the appearance of the carboxylate anion. And the appearance of a new very weak absorption band at 3571.69 cm^{-1} is the result of the dipole interaction of halogen-substituted compounds containing a carbonyl group and a negatively charged chlorine atom [6].

After exposure to chloric acid, a precipitate formed in the oil, which, according to TEM data, has a dense, chaotic structure, consisting of crystallites combined into large agglomerates, the size of which is $70\text{--}90\text{ }\mu\text{m}$ (Fig. 2). The elemental composition of crystallites (table) of spectra 1, 3, 4, 6, 7, and 8 in Fig. 2 indicates a predominant carbon content ($82.9\text{--}88.4\%$), as well as a relatively high

oxygen content (4.5–11.6%), and an insignificant the content of other elements: sulfur (1.9-3.5%), calcium (1.2-3.5%), zinc (0.4-1.5%), phosphorus (0.2-0.3%), sodium (0.1%), iron (0.1%), magnesium (0.1%), aluminum (0.1%) and chlorine (0.1%). In addition, the EDX spectra assigned to the solid phase indicate an uneven distribution of some of them.

Table: *Elemental composition of crystallites (Fig. 2)*

Specters	Contain of elements, % weight										
	C	O	S	Ca	Zn	P	Na	Fe	Mg	Al	Cl
1	84.0	11.6	2.1	1.5	0.4	0.2	0.1	-	0.1	-	-
2	87.2	5.3	3.3	2.9	1.1	0.2	-	-	-	-	-
3	86.9	4.6	3.1	3.1	0.8	0.2	-	-	0.1	0.1	0.1
4	84.4	11.1	1.9	1.6	0.6	0.2	-	0.1	0.1	-	-
5	90.2	6.6	1.5	1.1	0.5	0.1	-	-	-	-	-
6	86.7	4.5	3.5	3.5	1.5	0.3	-	0.1	0.1	-	0.1
7	86.3	7.8	2.6	2.4	0.6	0.2	0.1	-	-	-	-
8	85.9	10.7	1.4	1.2	0.5	0.2	-	-	-	-	0.1

So, for example, in spectrum 1 relative to spectrum 6, the oxygen content is 2.6 times higher, while sulfur is 1.7 times higher, calcium is 2.3 times higher, zinc is 3.8 times lower, and phosphorus is 1.5 times lower. According to TEM data, the size of the agglomerate from which spectrum 6 was taken is more than 8 times larger than the size of the agglomerate to which spectrum 3 belongs. This indicates that spectrum 1 contains a less condensed, intermediate form. According to this principle, the EDX spectra of all agglomerates can be divided into 2 phases: less condensed (spectra 1, 4, and 8) and more condensed (spectra 3, 6, and 7). But, considering the close elemental composition of these phases, it becomes obvious that the precipitate formed during regeneration is formed both due to the condensation of polymerization products of high-molecular compounds and fragments of ash additives, and compaction of a finely dispersed graphite-like structure.

At the same time, the presence of sodium, iron, magnesium, aluminum and chlorine was not detected in the EDX spectra 2, 5 (transparent areas representing the oil phase) (Fig. 2). This indicates that the separated phase of the oil has a qualitative composition different from the sediment, and the fact that the latter includes components of the main ash additives allows us to conclude that the conclusion about the mechanism of coagulation of highly dispersed particles, which was noted earlier in is correct [4,5].

During the analysis of the results obtained, it was noted that molybdenum and barium are absent in the composition of the oil and sediment, which, according to the data of [7], are included in the composition of the additives of the original engine oil, but along with this, carbon and aluminum appeared, and a high oxygen content was noted, and both of these facts are probably related to the exploitation of the operating conditions of engine oil: partial production of additives in the first case and the appearance of products of thermal and oxidative destruction of hydrocarbons, as well as wear on the surfaces of metal engine parts.

At the same time, sulfur, calcium, zinc and phosphorus are retained in the oil, and this speaks in favor of the preservation of alkylphenol additives [8, 9].

IV. Discussion

In the course of the spectroscopic studies of ADDINOL Super Light 0546 engine oil, it was found that the composition of ADDINOL Super Light 0546 engine oil includes aliphatic

hydrocarbons with long chain branching, polyorganosiloxanes, and esters of dicarboxylic acids. The results of the research indicate that changes occur during the operation of ADDINOL Super Light 0546 engine oil: vinyl oxygen-containing compounds are formed, the structure of polyolefins changes, and acid-type compounds appear. It was found that the oil obtained during the regeneration of the spent ADDINOL Super Light 0546 sample with chloric acid was characterized by the restoration of the structure of polyolefins, the complete removal of succinimide additives while maintaining detergent-dispersant and extreme pressure additives, and the resulting precipitate is carbon-containing agglomerates, which contain components of succinimide additives.

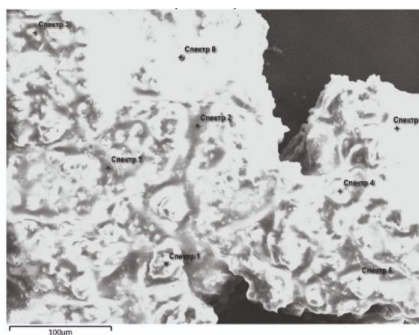


Fig. 2: Micrograph of a solid precipitate

The data obtained confirm the promise of the method of regeneration of used motor oils using chloric acid, which makes it possible to obtain a purified environmentally friendly product that is close in chemical composition to the original oil. Taking this into account, as well as the fact that the process is accompanied by the formation of not hard-to-recycle acid tar, but mineral sediment, the results obtained can become the basis for creating a waste-free technology for recycling used motor oil, solving environmental problems associated with the rational use of secondary resources.

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