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(RESEARCH ARTICLE)

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Thermolysis of petroleum oil and solubility of deposits

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Abstract

The article discusses the process of formation of deposits in the pipelines of the engine oil system and the factors affecting the conditions for their formation. The technological process of oxidation and the criteria for indicator parameters characterizing the thermolysis of used oil are shown. An extractive method is proposed that ensures the removal of deposits from the pipeline using special flushing process fluids based on regenerated petroleum oil.

To search for cheap and efficient hydrocarbon raw materials, regenerated petroleum oils were chosen from among the renewable resources of oil refining. The proposed process fluid was prepared on the basis of low-viscosity spent and then purified petroleum oil. The viscosity of the petroleum oil was adjusted with the addition of petroleum kerosene or diesel. Diluted surfactant solutions were used as additives. and detergent additive (alkali metal salts). It was revealed that in the oil system of an automobile engine at high temperatures (200-350 ^{0}C) oil thermolysis occurs, and the resulting deposits contain asphaltenes, carbons and carboids. The efficiency of dissolution of deposits in the mixture under study at low temperatures and the concentration of surfactants were revealed. The dependence of the interfacial tension on the concentration of various surfactants is shown. The limiting amounts of the content of the constituent components are found and the ratio of oily extract, from deposits of oxidized oil, is selected.

As a result of the tests, it was found that the washing liquid reduces the interfacial tension between the surface of the pipes and deposits and leads to an increase in the movement of the liquid. It has been established that the process of washing off deposits depends on the composition of the deposits, as well as on the composition of the oily extract. The optimal mode and prescription composition of the flushing liquid has been selected. The efficiency of washing off the studied liquid with other means is shown, while it should be noted that this liquid has a simple component composition and is much cheaper than other means.

Key words: Oil thermolysis; Deposits of oxidized oil; Regenerated petroleum oil; Interfacial tension; Oily extract; Surfactant

1. Introduction

Lubricants are often complex mixtures of chemicals whose main component is a hydrocarbon base oil. Base oils are usually derived from mineral oil and are classified by quality from groups I to IV, the standards for which are determined by the American Petroleum Institute. The higher the group number, the more refined the base oil will be, [1]

Oil oxidation is a chemical process where oxygen reacts with oil molecules to form a range of different chemical products such as carboxylic acids. The rate of oxidation depends on many factors and on temperature. With every ten degree increase in temperature, the oxidation state doubles. Deposits on the surfaces of internal combustion engine partsre divided into three main types - deposits, varnishes and sediments (sludge) [2].

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Nagar - solid carbonaceous substances deposited during engine operation on the surfaces of the combustion chamber (CC). The product of complete or partial combustion, resulting in the formation of soot.

The composition of the soot depends on the composition and properties of the burning fuel and oil. Thus, when working on leaded gasoline, approximately 50% of the soot is made up of lead compounds. The main elements that form soot when running on unleaded gasoline are carbon (up to 75%), oxygen (up to 20%) and hydrogen (up to 5%).[3]

Lacquer is a product of the change (oxidation) of thin oil films that spread and cover the parts of the cylinder-piston group (CPG) of the engine under the influence of high temperatures. The greatest harm to the internal combustion engine is caused by varnish formation in the area of the piston rings, causing the processes of their coking (deposition with loss of mobility). Lacquers, deposited on the surfaces of the piston in contact with oil, disrupt proper heat transfer.Sludge - precipitation formed in the internal combustion engine, (internal combustion engine) Sludge is a mixture of liquid substances, oxidized oil , the properties and quality of engine oil have a decisive influence.

The oxidation of hydrocarbons is subject to the theory of peroxides by A.N. Bach and K.O. Engler, supplemented by P.N. Chernozhukov and S.E. Crane. Oxidation of hydrocarbons, in particular, in ICE engine oils, can proceed in two main directions, presented in Table 1. In this case, the result of oxidation in the first direction is acidic products (acids, hydroxy acids, estolides and asphaltogenic acids), which form precipitation at low temperatures; the result of oxidation, in the second direction are neutral products (carbenes, carboids, asphaltenes and resins), from which either varnishes or carbon deposits are formed in various proportions at elevated temperatures.

Table 1 Oxidation products of engine oil in the engine (ICE)oil system.[3]

Hydrocarbon oxidation	
Hydrocarbons and peroxides	
At low temperatures (sour foods)	**At elevated temperatures. (neutral products)**
Acids	Resin
hydroxy acids	Carbenes
Estolids	Asphaltenes
Asphaltogenic acids	Carboids

A laboratory express method has been developed for modeling the aging of motor oils in a diesel engine, taking into account the catalytic oxidative thermolysis of motor oil in the presence of soot.[4]; .[5];

Influence of soot / soot PM-75,.on the change in the content of the hydrocarbon composition during the oxidation (3 h) of M-14 oil (before and after centrifugation.) Table2

Table 2 Change in the content of the hydrocarbon composition during the oxidation of oil M-14

Name of hydrocarbons	**Hydrocarbon composition, % (mass):**	
	Oxidized base oil M-14	**base oil M-14 after separation from soot**
Naftsno- paraffin ultraviolet	48.22	63.06
Aromatic u/v:		
Monocyclic	19.69	11.11
bicyclic -	7.33	7.66
Polycyclic	9.35	9.01
Resins	6.76	2.25
Asphaltsny	8.65	6.91

The study of the group hydrocarbon composition of the oxidized oil showed that mono- and polycyclic aromatic hydrocarbons, resins and asphaltenes are predominantly adsorbed on PM-75 soot. [four}.

Many companies are interested in the production of special flushing fluids, one of which is the German company Liqui Moly. These flushing fluids are mineralized and contain calcium as an additive, as well as zinc and phosphorus to prevent wear (Table 3).

- Liqui Moly has been producing specialized formulations for safely flushing the oil system for over 50 years. Products are sold not only in Germany, but also in more than 120 countries around the world, and the formulas are adapted to the specifics of regional operation.
- GUNK Motor Flush MF15ER - super concentrated 5-minute engine flush. The manufacturer recommends pouring GUNK Motor Flush into the engine before changing the oil. start the engine and let it idle for 5 minutes.
- Hi-Gear Motor Flush HG2204 - 5-minute engine flush for high mileage vehicles. It is stated that the high-performance formula used in the Hi-Gear HG2204 flush is designed specifically for high-mileage engines with heavy contamination, and allows you to remove most of them, including from the engine oil pan.
- Flushing liquids are not produced in Georgia.

Table 3 Flushing fluids for pipelines oil system [6]

No.	**Flushing fluid**	**Addition**		
		Washing	**Wear-preventive**	
		potassium, Camg/kg	**Zink Zn,mg/kg**	**Phosphorus P,mg/kg**
1	Liqui Moly Oil-Schlamm-Spulung	2399	1946	2050
2	GUNK Motor Flush MF15ER	1	0	4
3	Liqui Moly Engine Flush	772	1980	1978
4	Liqui Moly Pro-Line Motor Spulung	780	2181	2179
5	Hi-Gear Motor Flush HG2204	1682	0	7
6	RESURS	11	6093	6044

The purpose of this work is to develop and create effective, cheap and safe means (liquid) for removing deposits of oxidation products from the engine oil system.

2. Material and methods

The object of the study was deposits from the oil system of a car engine. The deposit is a product of thermolysis, oil, an oxidized deposit, black in color, consisting of soot, varnish and sludge. The formation of deposits in the engine oil system is caused by the operation mode in thermal oxidation conditions niya, as well as the composition and quality of the original engine oil

Based on the component composition of the oil, a solid, plastic deposit is formed on the pipeline wall, which increases with time and interferes with the free movement of the oily liquid. The quantitative and component composition of the oxidized oil has been studied and shown and a comparison is given Ni¬¬¬tel'naya characteristic in relation to the composition of the deposits of the main oil pipeline. The deposit was subjected to laboratory analysis and the physical and chemical parameters of the test samples were determined. (Tables 3 and 4).

Unlike the main oil pipeline, the composition of the soot of oxidized oil of the engine system includes: products of hydrocarbon oxidation(resins, asphaltenes, carbenes, carboids)

The mechanism and method for removing deposits from pipelines is associated with hydrophilization of the pipeline surface and a decrease in the viscosity of the deposit, which is achieved using the extraction method to destroy and dissolve deposits of oxidized oil. To remove deposits of oxidized oil, we have proposed a complex technological liquid

that provides complete destruction of the oxidized deposit in the presence of surfactants. Regenerated petroleum oil was selected as the constituent components of the process fluid. solvent and washing additives, surfactant solutions.[9]

Regenerated petroleum oil was selected as the constituent components of the process fluid. solvent and washing additives, surfactant solutions.

Table 4 Composition and properties of soot [8]

№	Components	In operation and trunk pipelines, %	In vehicle engine pipe, %
1	Paraffines-naftens	45-60	
2	Asphaltenes	10-15	
3	Tars	20-25	
4	Water and mechanic inclusions	5-10%	
5	Motor oil		50-80
6	Water		5-35
7	Fuel		1-7
8	Oxyacids		2-15
9	Asphaltenes		0.1-1.5
10	Carbenes and carbids		2-10

2.1. Waste and reclaimed petroleum oil

The main detergent for our research is waste oil is a brown oily liquid with a density at 20 °C of 0.8862 – 0.920 g/cm^3.

Table 5 Physical and chemical parameters of regenerated petroleum oil

Parameter SAE 15W-40	Test method	Refinedoil	Norm
Density 20 ^{0}C g/cm3	ISO 3675 /ASTM D1298	0.8862	0.885
Kinematic viscosity 40^{0}C mm2 /sec	ISO 3104/ ASTM D445	96.0	106 -112,5
Kinematic viscosity100 ^{0}C mm2 /sec	ISO 3104/ ASTM D445	7-8.01	14,1 -14,85
Viscosity index	iSO 2909/ ASTM D2270	>100.	136/137
Total alkalinity mg.kon/g	ASTM D2896	7.8	10,12 –11,98
Flash point ^{0}C	ISO 2592/ ASTM D92	220	228
Curing temperature ^{0}C	ISO 3016/ ASTM D97	-18	- 25

It should be noted that the waste petroleum oil, based on the degree of contamination, was purified by extractive and adsorption methods. The results of technological studies of purification and regeneration of petroleum oil are given in the scientific report of the grant project GNSF496-7-201 2011. Georgia**.**

2.2. Water content

Hydrometer device, to determine the water content

- (express method)
- Definition method.

An express method using anhydrous magnesium sulfate (MgSO4) was used to determine the water content in oil deposit samples as well as regenerated oil. Oils in a volume of 25 ml. pouring into the tank with a thermometer. The starting temperature t1 is measured and MgSO4 is added in an amount of 0.2 g. After that, the temperature t2 is again fixed and the difference ΔT \u003d t1 - t 2 is calculated then with a graduated straight line. Fig. 2 Find the corresponding water content value. In % - max [9][10].

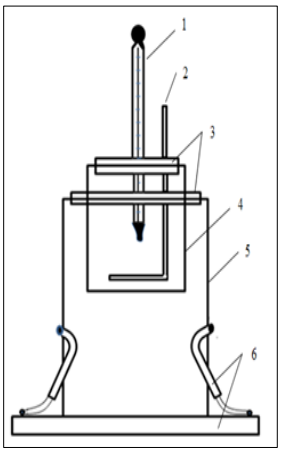

Figure 1 Moisture meter to determine the content Water in lubricants (express method)

2.3. Detergents and dispersants additives [12] [13]

Detergents and dispersants are surface-active substances (surfactants) whose molecules contain active polar groups. As a surfactant was selected: non-ionic surfactant Alkan de202; and anionic surfactant Sulfanol. It is an alkylsulfonate, fatty acid ester

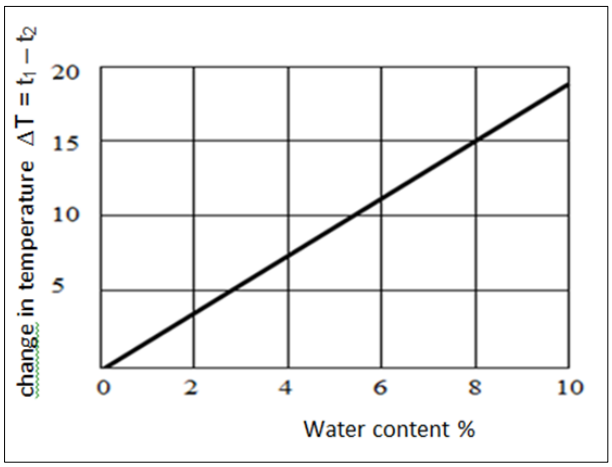

Figure 2 Graph for determining the water content. % : ΔT = t1 - t2

An accelerated method for determining the acid number of used and reclaimed oils.

Definition method: Pour 10 ml of the tested oil into a glass tube. then add neutralized ethyl alcohol 10 ml. benzene in a ratio of 10.\ 1 tube is tightly closed and shaken for 2 minutes. Then add an accelerated method for determining the acid number of used and reclaimed oils.

2.4. Determining the acid number

Pour 10 ml of the tested oil into a glass tube. then add neutralized ethyl alcohol 10 ml. benzene in a ratio of 10.\ 1 tube is tightly closed and shaken for 2 minutes. Then add 20 drops of the nitrosone yellow indicator and an alcohol solution of KOH until the color changes [9].

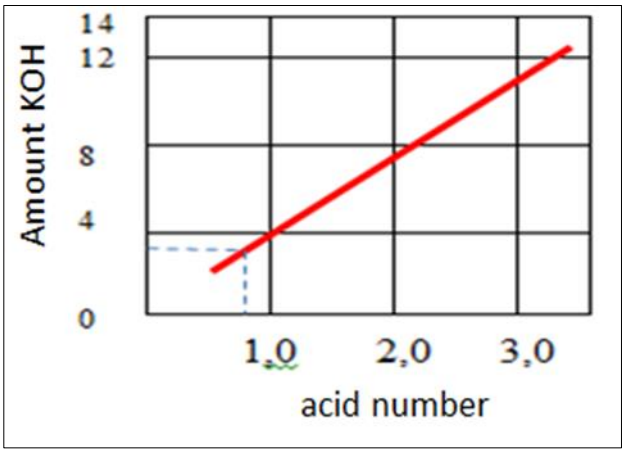

Figure 3 Dependence of the acid number of the oil on the amount of alcohol solution of KOH used to neutralize 10 cm3 of the oil product [9].

There are a number of field tests that allow a high degree of accuracy to show varnish tendencies. These tests include the following tests

Test with blottingpaper. Apply a couple of drops of used oil to regular blotting paper (found in lab kits). If it is not at hand, you can test on the back of a regular business card. Let the drops soak into the paper for two hours. If a dark or brownish spot remains in the center of the formed oil absorption zone, this may indicate the presence of insoluble carbon or oxides.

3. Research results and discussion

The experiments were carried out in the conditions of the educational laboratory of the Faculty of Technology of the Belarusian State University. Samples of deposited oxidized oil were weighed on an electric balance in the amount of one gram (1 + 0.2 g). Weighed samples were prepared in the form of a tablet and transferred in baskets attached to a flask (Erlenmeyer). viscosity. A solution of surfactants of various classes was chosen as a dispersant. anionic active Sulfanol (0.05%) and non-ionic, Alkan de202 (0.05%). as well as their mixtures. (0.1%) The extraction lasted about 2 hours, at ambient temperature, without heating. The extraction process was controlled by gravity. (weight method) After the end of the extraction Physical parameters are determined: washing power, surface tension coefficient, viscosity and density.

3.1. The efficiency of washing was calculated by the formula [15] [14]

$$E=[(M_1-M_2)/M_1] \times 100\ \%$$

Where:
M1 is the mass of the ARPD taken for the experiment, g;
M2 - the mass of the ARPD residues in the basket after experiment, Mr

3.2. Surface tension was determined on a stalagmometer

The surface tension of surfactant solutions was determined by the stalogrammetric method. For this purpose, solutions of different concentrations of surfactants were prepared in the range (0.125 – 1.0%), the results are shown in Table 6. The results showed that sulfanol has a surface tension 2 times less than alkan DE 202.

Studies have shown that the sulfanol solution had the lowest surface tension coefficient, so it was given preference as an additive to flushing fluids .

Table 6 The results of determination of surface tension at the interphase surface, in presence of various class SAS [11]

Concentration of SAS, %	Surface tension10–3n./m 2.	
	Sulfanolum	alkan DE 202
1.0	0.93	.,74
0.5	1.83	5.26
0.25	2.40	7.00
0. 125	3.61	8.90
Without SAS	44	

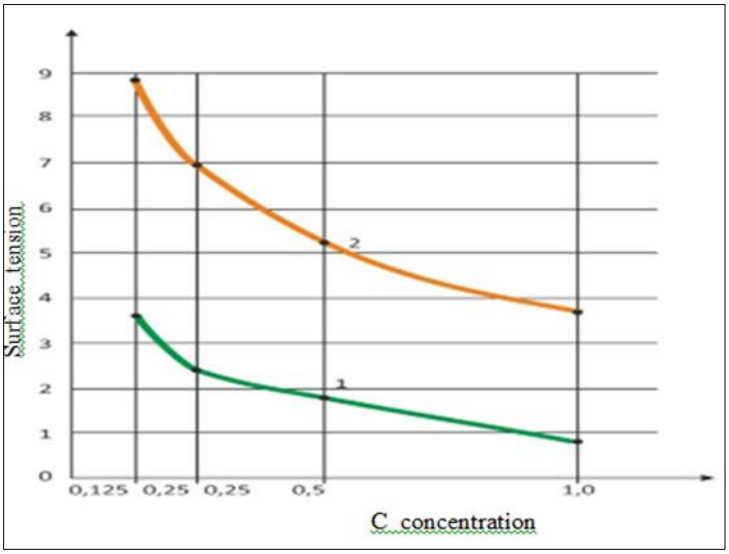

Figure 4 Dependence of surface tension coefficient on the concentration of the investigated reagent. 1. sulfanol 2. alkane DE 2 02

3.3. Surface tension

Determination ofinterfacial tensionSurface tension of fluid is calculated with formula:

$$\sigma = m\ g\ /\ \pi\ D\ n$$

Where;
m-total weight of drops; gπ
g-free falling
acceleration -9.8 m/sec^2;π -3.14
D-0.35 cm; capillary diameter;n-number of drops.
σ - surface tension coefficiaent, n/m ^{2};

3.4. Kinematic viscosity

The kinematic viscosity was determined by the formula:

$$V = \tau\ K;$$

Where;
V- kinematic viscosity -; mm^2/ second;

τ-expiration time; second ;
K-0.1006 ;Constant of a viscometer ; d= 0.99 .;
(d= 1.47 ;K = 0.2010);

3.5. Determination of the density of a liquid

$$d = d_t + \alpha(t-20)$$

Where;
dt is the density of the liquid at the test temperature
d20 - density at 20^0 C
α- correction factor

In Fig. 5 and Fig. 6. The limiting quantities of the content of the constituent components are determined and selected. oil extract ratio, from oxidized oil deposits

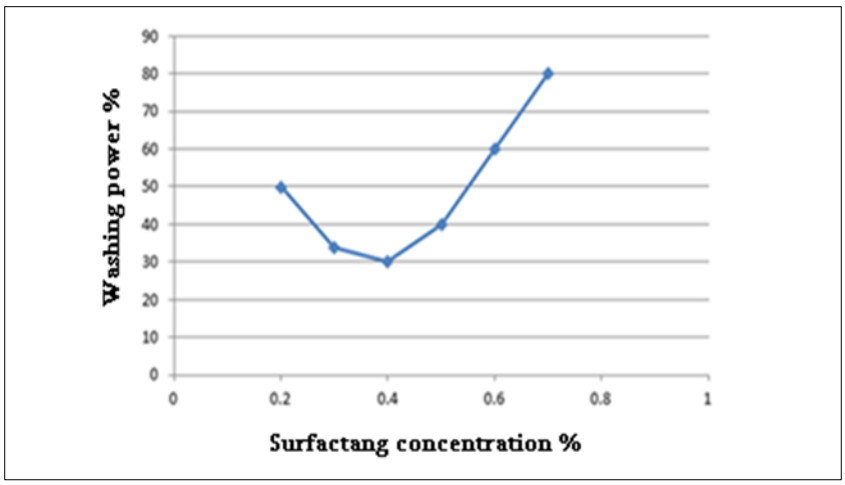

Figure 5 Determination of the limiting concentration reagent Surfactant solution. when exposed tu washing liquid on

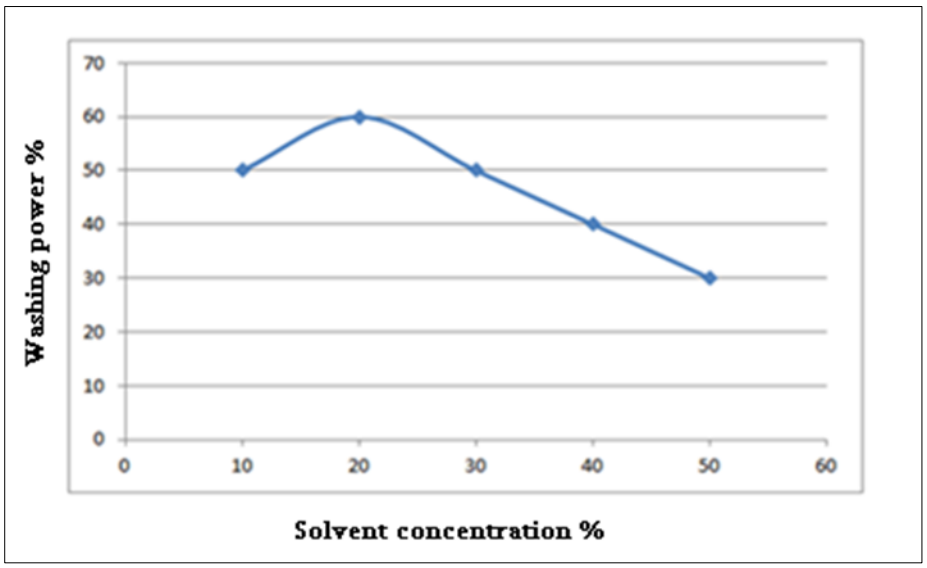

Figure 6 Influence of the composition of the washing liquid on the solubility at different concentrations of Solvent

Table 7 Composite mixtures and detergent efficiency in time

№	interval contact time	Washing efficiency of the test subjects samples over time in % (at a ratio of 1/30)			
		used oil	Composition Oils Solvent diesel	Composition Oils Solvent kerosene	Composition oils kerosene Surfactant 0.1 %
1	20	40	50	60	70
2	40	50	70	70	80
3	60	60	80	90	90
4	80	60	80	90	90

Based on the laboratory tests, the tested one was selectedeffective composition of the washing liquid:[petroleum oil based extractant + kerosene + surfactant]

4. Conclusion

- The process of thermolysis of petroleum oils and the products of deposition of oxidized motor oil have been studied and its chemical composition has been established.
- Delayed dissolution efficiency has been found to be achieved with dilute concentrations of oil in the cleaning fluid composition.
- The limiting amounts of the content of the constituent components have been established and the ratio of oily extract, from deposits of oxidized oil, has been improved.
- It was found that a mixture of surfactant solutions not only reduces interfacial surface tension, deposits, but also actively participates in the destruction of deposits of oxidized oil
- The dependence of interfacial tension on the concentration of various surfactants and their mixtures is shown.
- As a result of tests, it was found that the washing liquid reduces the interfacial tension between the surface of the pipes and deposits and leads to the hydrophilization of the movement of the liquid.
- It has been established that the process of washing off deposits depends not only on the composition of the deposits, but also on the composition of the composition of the oil extract. The optimal mode and prescription composition of the flushing liquid has been selected.
- The similarity and efficiency of washing the test liquid with other washing liquids were revealed.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

No conflict of interest.

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