

UDC 52.45.19

DOI: 10.15372/CSD2019183

Purification of Used Motor Oils by Ozone Treatment

S. A. SEMENOVA, YU. F. PATRAKOV

*Federal Research Center of Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia**E-mail: semlight@mail.ru*

Abstract

The data on the effect of ozonation on the component composition and chemical properties of spent mineral engine oil are presented. It is shown that as a result of ozonolytic treatment, the relative content of aromatic and unsaturated compounds decreases in the composition of the waste oil, with an increase in the proportion of low-boiling components in the form of alkyl, alkyl ether and alicyclic structures. The content of aliphatic carboxylic acids, ethers and esters with linear and cyclic structure, lactones and anhydrides, which replenish the composition of resinous products, increases. The possibility of waste oil purification from mechanical impurities and resinous products by ozonation was revealed, and the optimal process conditions were determined, which correspond to ozone consumption of about 11 g/kg. The products of ozonation of the used engine oil - purified oil, resins, mineral deposits - can be reused in chemical, petrochemical and construction branches of industry as raw materials or their components.

Keywords: used motor oils, regeneration, ozonation, oxygen-containing resins

INTRODUCTION

The trend to the rational utilization of natural resources and sharpening of ecological problems connected with the absence of controlled collection of wastes from petroleum processing brings around the task to utilize these wastes or to use them repeatedly. In Russia, with 2.8–3.2 mln t of lubricating oil manufactured annually, less than 50 % of collected wastes are subjected to further treatment; the management of collected wastes is practically absent [1]. In western countries, the USA and Australia the major fraction (>80 %) of collected worked out motor oil (WMO) is utilized through combustion as components or substituents of fuel oil or is repeatedly involved into production to manufacture new basic oil by mixing with crude oil [2].

In smaller amounts, WMO may be processed as additives into polymers to manufacture liquid hydrocarbon products by means of pyrolysis [3];

substituents of bitumen together with polymers in the production of binders [4]; components of asphalt concrete mixtures in road construction; grease for rough frictional units, reinforced concrete molding tools; it may also be used to treat coal against freezing and weathering during transportation, to strengthen the sand layer of soil *etc.* [2, 5] or be regenerated.

Regeneration is the most technologically complicated process of WMO processing, which allows one to use it as a basis for obtaining both new lubricating oil and fuel similar to petroleum in composition. The production of hydrocarbon products on the basis of oil wastes is economically more profitable than crude oil processing. For instance, 1 kg of lubricating oil may be obtained through processing 1.6 kg of the wastes of petroleum products or 79 kg of crude oil [5]. So, after the removal of contaminating particles (the particles of dust, carbon, metals, oxidation products)

and recovery of the performance characteristics, WMO may be considered as the raw material basis for the production of valuable hydrocarbon products.

Technologies that are used for WMO regeneration are based on various physical, physicochemical and chemical principles. Physical methods of purification are used most frequently: settling, centrifuging, filtration, distillation of fuel fractions, washing with water, vacuum distillation. Physicochemical methods used for this purpose involve the coagulation of pollutants, contact purification with bleaching clay and activated adsorbents, selective purification with propane, phenol *etc.* [6]. The chemical methods of WMO purification include sulphuric and alkaline treatment; their major disadvantages are the formation of difficult-to-utilize wastes (acid goudron, sludge, waste waters).

Treatment with ozone is one of the oxidative methods that proved itself to be useful in petroleum chemistry and chemistry of organic compounds. Unlike for widely used classical oxidizers (mineral acids, hydrogen peroxide, potassium permanganate, molecular oxygen, *etc.*), ozone possesses reactivity and selectivity to definite types of bonds and heteroatoms [7]. Ozonation does not require the high concentration of the oxidizer, the presence of catalysts, increased temperature or pressure, *etc.* [8, 9].

The goal of the work was to study the possibility to purify WMO by means of treatment with ozone and evaluation of the composition of resulting products.

EXPERIMENTAL

The object of investigation was WMO sampled from collecting tanks at the Kuzbass coal mining open pits exploiting heavy-duty dump trucks. Oil characteristics were determined experimentally according to the adopted procedures: density at 20 °C (GOST ISO 3675–2014) – 905 kg/m³, kinematic viscosity at 50 °C (GOST 33–2016) – 40.9 mm²/s, water content (GOST 2477–2014) – 1.5 %, ash content (GOST 1461–75) – 1.2 %, mechanical impurities (GOST 6370–2018) – 1.0 %. On the basis of the data obtained, the WMO sample under investigation corresponded to GOST 21046–86 Waste Oil Products.

The treatment of WMO sample (100 ml) with ozone was carried out at a temperature of 25 °C and pressure of 1 atm in a thermostatic rotating

reactor with the help of a laboratory ozonizer of Shenzhen Blueocean Industry Co., Ltd (China) with the capacity up to 50 W. Ozone concentration was controlled by varying the power of the ozonizer. The gas to be ozonized was high-purity gaseous oxygen of 4.0 grade. The rate of gas flow was 150 ml/min. Ozone concentration was determined with the help of IKO-02 ozonimeter (JSC MELP, Russia) (absorption by ozone in the UV spectral region at $\lambda = 254$ nm). The overall experimental error of the measurement of ozone concentration was ± 2.5 rel. %. In the discussion of results, we took into account the data on specific ozone consumption (SC) (g/kg) – the amount of ozone that actually entered the reaction with the components of WMO.

The WMO samples treated with ozone with SC more than 11 g/kg were separated after settling into a transparent oily layer and the precipitate. The initial WMO sample and the samples treated with ozone at a low SC were not purified from mechanical impurities by settling. Separation of the products was carried out as follows: oil purified from mechanical impurities was poured off, the black oily precipitate was washed with *n*-hexane to remove hydrocarbon products, and filtered. A mixture of insoluble and tarry products was extracted with acetone to separate resins. The products were oil purified from tarry and mechanical impurities, oxygen-containing resins, and a hydrophobic powdered black-coloured precipitate. The yield of resins was 2–3 mass % depending on ozone SC.

For the purpose of evaluating the fragmentary composition, we used base mineral oil manufactured by Lukoil company as a reference sample for WMO purified from tarry and mechanical impurities.

IR spectra were recorded with an Infralyum-FT-801 Fourier spectrometer (Russia) within the region 400–4000 cm⁻¹. The intensities of absorption bands were normalized over the band at 1460 cm⁻¹ which characterizes the bending vibrations of C–H bonds in alkanes. The degree of oil oxidation (K_o) was calculated from the ratio of the total intensity (a sum of integral optical densities (D)) of absorption bands of oxygen-containing alcohol and ether (1240 cm⁻¹) and carboxylic (1710 cm⁻¹) groups to the total intensity of the absorption bands of CH_n aliphatic (1920 cm⁻¹) and CH aromatic (3040 cm⁻¹) groups:

$$K_o = (D_{1240} + D_{1710}) / (D_{1920} + D_{3040})$$

Thermal analysis of WMO was carried out with the help of Netzsch STA 409 thermoanalyzer (Germany): sample mass was 10–20 mg, heating to 600 °C at a rate of 10 °C/min in helium.

The ^1H and ^{13}C NMR spectra of the products were recorded with a Bruker Avance AV 300 spectrometer (Germany) at a frequency of 75 MHz with the application of the standard procedure of cross-polarization and magic angle spinning (CPMAS); deuterated chloroform was used as the solvent. Identification and quantitative interpretation of the spectra were carried out according to the procedures described in [10, 11].

Microanalysis of the elemental composition of the solid residue of WMO was carried out with a scanning electron microscope JEOL JSM-6390 LA (Japan) equipped with an X-ray spectral analyzer JED-2300 as the analytical attachment.

RESULTS AND DISCUSSION

Effect of treatment with ozone

Characterization of initial and ozone-treated WMO samples is presented in Table 1. Depending on the power of the electric discharge in the laboratory ozonizer, it is possible to obtain reactive gas with ozone concentration 40–120 mg/L. The maximal concentration of ozone in the ozone-oxygen mixture is achieved at the power of 40 W, and it changes only slightly with subsequent toughening of conditions. An increase in ozone consumption for the reaction with hydrocarbons in WMO is achieved by increasing the time of ozonation. Taking into account the difference between ozone concentrations at the inlet and outlet of the reactor, SC of ozone for the reaction with WMO components was 3.5–20 g/kg (see Table 1).

With an increase in the amount of absorbed ozone, the acid number (AN) of WMO increases from 0.35 mg/g for the initial sample to 1.30 mg/g in oil with the maximal SC of ozone (see Table 1). The values of K_o increase by a factor of 2–3 depending on the degree of WMO ozonation (see Table 1), which provides evidence of an increase in the total amount of ether, hydroxyl and carboxyl groups in its composition.

In addition to chemical composition, ozonation also causes changes in the rheological properties of WMO. For instance, at the initial stage of ozonation, a slight increase in the kinematic viscosity (KV) of the product is detected, which may be due to the formation of oxygen-containing compounds with larger molecular mass (resins) in WMO. Further on, up to ozone SC 7.5 g/kg, KV gradually decreases, and oil after settling remains black-coloured, which is explained by the presence of dispersed carbon and metal inclusions. When ozone SC reaches 11 g/kg, the WMO sample becomes transparent but is still brown because of the presence of oxygen-containing aromatic and unsaturated compounds. After the deposition of mechanical impurities, KV of ozonized oil becomes substantially lower (by ~20 %) than that of the initial WMO sample. Further increase in ozone SC has no significant effect on the change of KV and is depicted only in the variations of AN of the product (see Table 1).

It is reasonable to assume that secondary oxidation processes taking place in the case when high ozone doses are used to promote the clarification of WMO. Oxidation initiated by ozone may proceed with bond rupture and with the formation of vapour-phase (H_2O) and gaseous (CO , CO_2) products, and lead to the formation of inter- and intramolecular C–C and C–O links [7], which

TABLE 1

Characteristics of initial and ozone-treated WMO samples

Charge power, W	Duration of treatment with ozone, h	Specific consumption of ozone, g/kg	Acid number, mg/g	Oxidation degree K_o	Kinematic viscosity, mm^2/s
0	0	0	0.35	0.06	40.9
25.0	1	3.5	0.59	0.12	41.2
30.0	1	5.0	0.65	0.15	40.7
32.5	1	6.5	0.76	0.22	39.9
35.0	1	7.5	0.70	0.18	39.2
30.0	3	11.0	0.73	0.11	32.2
35.0	3	15.0	0.98	0.14	32.7
40.0	3	20.0	1.30	0.12	32.8

leads to an increase in the molecular mass of the compounds and to the formation of tarry oxygen-containing products. Tarry and oil-insoluble products precipitate with time, aggregating carbon and metal impurities of WMO, which provides clarification of the product and causes a decrease in its KV (see Table 1). So, the use of ozonation promotes the purification of WMO from metal and sooty products of the operation of automobile engines.

IR spectroscopy

In the IR spectra of WMO at the initial stage of ozonation (SC of ozone p to 6 g/kg), the intensities of absorption bands related to aromatic CH bonds (3040 cm^{-1}) decreases, and the intensity of absorption bands of methyl, methylene ($2920, 1380, 720\text{ cm}^{-1}$) and alicyclic (970 cm^{-1}) fragments increases. The intensity of absorption bands of oxygen-containing groups increases, too: O-H groups of alcohols and phenols (3400 cm^{-1}), C=O of lactones and anhydrides (1770 cm^{-1}), C=O of aliphatic (1730 cm^{-1}) and aromatic (1710 cm^{-1}) acids, aromatic ketones (1650 cm^{-1}), C-O of ethers, furans and lactones (1260 cm^{-1}), S=O of sulphoxides ($1300, 1150, 1050\text{ cm}^{-1}$) (Fig. 1, Table 2). An increase in the intensity of the band at 1600 cm^{-1} , which characterizes the absorption by aromatic C=C bonds, may be due to the superposition of absorption from conjugated C=O groups formed during ozone treatment, as well as from diketones in the enol form [7].

With ozone SC 6.5–7.5 g/kg, the intensities of the absorption bands of above-indicated structural groups and bonds in WMO pass through an extremum and then change in the inverse order

with definite monotony (Fig. 1). The samples with a high degree of ozonation (ozone SC above 11 g/kg) exhibit no pronounced changes in the intensities of absorption bands.

The IR spectra of resins revealed some features characterizing the fragmentary composition of the products of WMO oxidation (see Table 2): pronounced intensities of absorption bands related to stretching ($2920, 2850\text{ cm}^{-1}$), bending ($1460, 1380\text{ cm}^{-1}$) and skeletal (720 cm^{-1}) vibrations of CH_n groups of aliphatic type, increased intensities of the absorption bands of cyclanes ($2990\text{--}3015,$

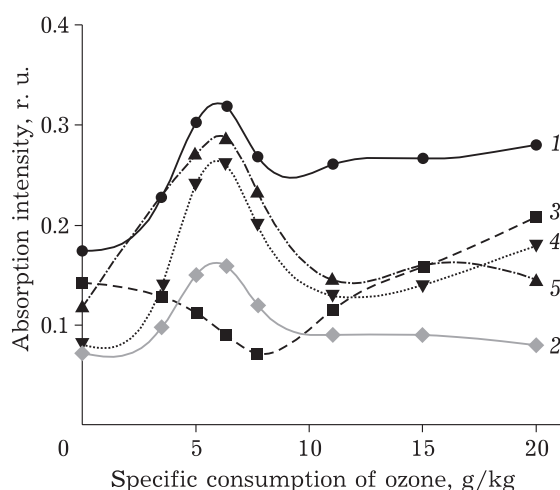


Fig. 1. Dependence of the relative intensity of absorption bands in the IR spectra of WMO: $(\text{CH}_2)_n$ groups of alkanes D_{720} (1), CH_2 groups of cycloalkanes D_{970} (2), CH aromatic groups D_{3040} (3), C=O groups of aliphatic acids D_{1710} (4), C-O groups of ethers and alcohols D_{1240} (5) on the conditions of ozone treatment. All intensities are normalized to the band at 1460 cm^{-1} .

TABLE 2

Normalized intensity of the characteristic absorption bands of some groups and bonds in the IR spectra of WMO samples (D/D_{1460}), rel. units

Parameter	3400	3040	2920	2670	1770	1710	1600	1380	1240	1150	970	720
	-OH	$\text{C}_{\text{ap}}\text{H}$	$\text{C}_{\text{ar}}\text{H}$	-OH	C=O	C=O	$\text{C}=\text{C}_{\text{ap}}$	CH_3	C-O	C-O	$\text{C}_{\text{naph}}\text{H}$	CH_2
Specific consumption of oxygen, g/kg:												
0	0.03	0.14	3.01	0.11	0.01	0.08	0.06	0.56	0.12	0.11	0.07	0.17
5.0	0.05	0.11	2.19	0.24	0.07	0.24	0.24	0.71	0.27	0.26	0.15	0.30
11.0	c.n. ^a	0.16	2.29	0.04	0.02	0.13	0.06	0.55	0.15	0.16	0.09	0.28
Resins	1.50	0.10	1.82	0.13	-	0.20^{1710} 0.30^{1650}	0.18	1.04	0.67	6.17	0.77	0.18

Note. Dash means the absence of absorption in this spectral region.

^a Weak intensity of absorption bands.

1030, 990, 910 cm^{-1}), and a weak absorption in the region of vibrations of CH and C=C bonds of aromatic rings (3040, 1610 cm^{-1}). This points to the high total content of aliphatic and/or alicyclic compounds in the resinous products. Oxygen-containing structures are represented mainly by cyclic ethers, ketals and acetals (1080, 1030, 980, 950, 880 cm^{-1}), free OH groups in polymeric structures (3370 cm^{-1}), enol and chelate OH groups (3200, 2760, 2720 cm^{-1}), aliphatic and aromatic (1730–1650, 1350, 880–860 cm^{-1}) acids and dimers of acids, as well as esters and lactones (1770, 1650, 1240, 1190 cm^{-1}).

NMR spectroscopy

The data on the relative distribution of hydrogen and carbon atoms in the structural fragments of hydrocarbons in oils and resins are presented in Tables 3 and 4. Normalized integral intensities of the major types of protons and carbon atoms in the components of WMO ozonation products in comparison with the base mineral oil were determined on the basis of the analysis of ^1H and ^{13}C NMR spectra. One can see that dominating components in mineral oils are aliphatic and naphthene hydrocarbons with the chemical shifts of

TABLE 3

Parameters of the fragmental composition of oil products according to the data of ^1H NMR spectra

Range of chemical shifts, ppm	Distribution of hydrogen atoms over structural fragments	Sample, rel. %		
		Base mineral oil	WMO purified from mechanical impurities and resins	Resins
0–1.0	CH_3 groups of saturated compounds and CH_3 groups in γ and more remote positions with respect to the aromatic ring	30.51	22.87	14.5
1.0–2.0	CH_2 groups of paraffin chains and cyclanes, CH_3 groups in β position to the aromatic core	67.74	70.98	4.81
2.0–2.25	CH groups of paraffin and naphthene fragments	0.46	1.54	0.15
2.25–2.8	CH_3 groups in α position to aromatic fragments	0.48	2.24	0.21
2.8–4.5	CH and CH_2 groups in α position to aromatic fragments, CH_2 and CH_3 groups at aldehyde and ether groups, CH groups at alcohols and ethers	0.28	1.18	75.17
4.5–6.0	Hydrogen atoms of olefin fragments	0.10	0.06	3.84
6.0–7.3	Hydrogen atoms of monoaromatic compounds	0.23	0.74	0.71
7.3–8.0	Hydrogen atoms of condensed aromatic rings	0.07	0.35	0.31
8.0–8.6	Hydrogen atoms of polycyclic and heteroatomic aromatic rings	0.05	0.05	0.10
8.6–10.0	H–C=O	0	0	0.12
10.0–12.0	O=C–OH	0	0.01	0.07

TABLE 4

Parameters of the fragment composition of oil products according to the data of ^{13}C NMR spectra

Sample	Range of chemical shifts, ppm								
	0–25	25–51	67–51	67–93	93–148	148–170	170–185	185–205	205–215
	Distribution of carbon atoms over structural groups, rel. %								
	CH_3	CH_2	CH_3O	$\text{C}_{\text{alk}}\text{O}$	$\text{C}_{\text{ar}}\text{H} + \text{C}_{\text{ar}}$	$\text{C}_{\text{ar}}\text{O}$	COOH, COO–	COH	C=O
Base mineral oil	22.6	75.0	0	1.2	0.7	0.4	0	0	0.1
WMO purified from mechanical impurities and resins	20.8	75.9	0.3	1.2	1.2	0.4	0.1	0.1	0
Resins	13.6	2.3	14.4	66.1	0.3	1.0	0.5	1.1	0.7

signals within the range 0–2.3 ppm (see Table 3). The fraction of hydrogen atoms in the aliphatic fragments in base oil reaches 98 rel. %. For the WMO sample purified from mechanical impurities and resins (SC of ozone 11 g/kg), this parameter is somewhat lower (95 rel. %) due to the distribution of some protons in aromatic (6.0–8.6 ppm) including alkyl-substituted (2.3–4.5 ppm) fragments. The major structural units of hydrocarbons in oils are CH_2 groups of paraffin chains and cycloalkanes (68–71 rel. %); the fraction of protons in CH_3 groups is equal to 25–31 rel. %. The content of hydrogen atoms in aromatic (6.0–8.6 ppm) and olefin (4.5–6.0 ppm) structures is insignificant – less than 1 rel. %.

According to the data of ^1H NMR spectroscopy, the distribution of the components of tarry products exhibits principal differences. The fraction of hydrogen atoms in paraffin and naphthene fragments (0–2.3 ppm) in resins is substantially lower than in oils, but the relative content of protons in olefin structures (4.5–6.0 ppm) increases noticeably. The major fraction of protons (75 rel. %) relates to CH_3 , CH_2 and CH groups at aldehyde, ether and alcohol groups (2.3–4.8 ppm). NMR spectra of resins exhibit the chemical shift of protons in carbonyl (8.6–10.0 ppm) and carboxyl (10.0–12.0 ppm) groups (see Table 3, Fig. 2).

Analysis of the data of ^{13}C NMR spectra of oils showed that the samples of base oil and WMO purified from mechanical impurities and resins (SC of ozone 11 g/kg) are identical in the

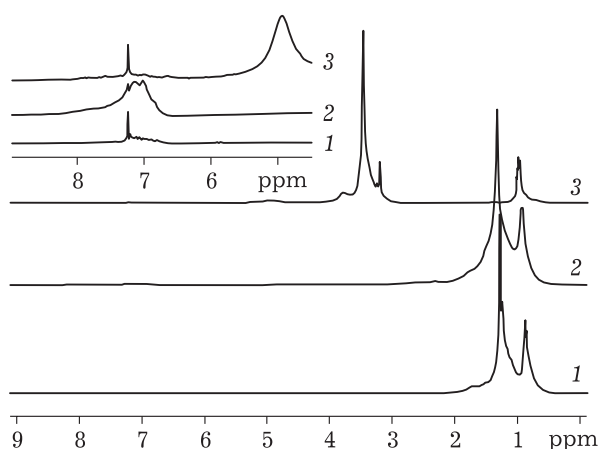


Fig. 2. The ^1H NMR spectra of base mineral oil (1), WMO purified by ozonation (2) and oxygen-containing resins (3). The insert shows the spectral region within the range 4.5–9.0 ppm.

distribution of carbon atoms, which is the evidence of the conservation of the hydrocarbon composition of oils after their operation, ozone treatment and separation of side products. The major fraction of carbon atoms (~98 rel. %) in oils are aliphatic (0–51 ppm). In tarry products, a large fraction of carbon atoms (66 rel. %) are in C–O bonds of aliphatic (alicyclic) structures (67–93 ppm), which is in agreement with the data of ^1H NMR and IR spectroscopy (see Tables 2, 3). A small part (~2 rel. %) of carbon atoms are incorporated into peripheral carboxylic, aldehyde and ketone groups (170–215 ppm) (see Table 4).

TABLE 5

Results of thermal analysis of WMO and the products of its ozonation

Sample	$(T_i - T_f)$, °C	T_{\max} , °C	V_{\max} , %/min	Δm , %		
				within temperature range, °C		
				25–340	340–600	25–600
WMO, initial	340–480	419.6	11.9	15.7	83.0	98.7
WMO purified from mechanical impurities and resins	285–445	381.0	10.0	31.8	67.1	98.9
Resins	120–287	197.7	4.6	59.4	35.0	94.4
	287–325	297.6	1.3			
	325–420	382.9	6.5			
Base mineral oil	370–470	445.2	18.5	3.7	95.8	99.5

Note. $T_i - T_f$ is temperature range between the start (T_i) and finish (T_f) of the major evolution of volatile products, T_{\max} is the temperature of maximal evolution of volatile products; V_{\max} is the maximal rate of evolution of volatile products; Δm is the loss of mass by samples within the corresponding temperature range.

^a 340 °C is the limit of distillation of light fractions for WMO (GOST 21046–86).

It is evident that the features of the composition of tarry products extracted from ozonized WMO are due to the effect of oxidative transformations of oils under the conditions of their operation and under the action of ozone. Oil oxidation is accompanied by the destruction of reactive bonds of hydrocarbons, partial dehydration, the formation of both the poorly soluble oxygen-containing compounds and the structures that are higher molecular, cyclic, linked through carbon-carbon and carbon-oxygen bridges, which form the basis of tarry products.

Thermal analysis

The transformations of the structural fragments of components in ozonized oils observed according to the results of IR and NMR spectroscopy are inevitably accompanied by the transformation of their fractional composition, which may be evaluated indirectly from the data of thermal analysis (Table 5).

The amount of products released from the clarified ozonized WMO sample (SC 11 g/kg) within the interval of the distillation of light fractions (<340 °C) increases substantially (by a factor of 2) in comparison with initial WMO. The interval of the major evolution of volatile products broadens (by 20 °C) and shifts to the lower temperature region of the process; the temperature (T_{\max}) and rate (V_{\max}) of the maximal evolution of products decrease. These changes provide evidence that the composition of WMO purified from resins and mechanical impurities is represented by a larger fraction of compounds with relatively low boiling temperature (T_b). These may be either oxygen-containing substances formed as a result of oxidation, destruction of aromatic and unsaturated compounds [7] or light hydrocarbons, the fraction of which increases as a result of precipitation of high-molecular tarry products.

Oxygen-containing resins isolated from the ozone-treated WMO sample under the conditions of thermolysis in the inert atmosphere exhibit the signs of oxygen-containing compounds (intense destruction of -OH, C-O and -C=O groups in the low-temperature region 120–325 °C) and the

hydrocarbon basis (decomposition within the interval 325–420 °C). The major mass loss (59.4 %) occurs within the low-temperature region of the process, which is the evidence of the high fraction of oxygen-containing groups in resins. A broad decomposition region, many plateaus and weakly pronounced peaks on the low-temperature maximum are the evidence of the diversity of types of oxygen groups and the forms of their bonding with hydrocarbon fragments of tarry products. The second maximum of the evolution of volatile substances during thermal destruction of resins coincides in the temperature with the major maximum of thermolysis of ozone-treated WMO, which points to the same type of hydrocarbon fragments in these products.

Elemental analysis of the mechanical impurities in WMO

The data on the elemental composition of the powdered residue isolated from WMO (Table 6) provide evidence of the presence of carbonaceous products (35.3 mass %), oxygen (23.9 mass %), most probably in metal oxides and salts (mainly iron (20.9 mass %) and aluminium (2.4 mass %), as well as sulphur (1.5 mass %), calcium (6.7 mass %) and silicon (5.6 mass %). The content of other metals (potassium, titanium, chromium, nickel, copper, zinc) does not exceed 1 mass %. The origin of these components is mechanical wear of the metal parts of engines, scale, components of additives, sand and clay.

Directions of the use of the products of WMO ozonation

Our previous investigations [12, 13] showed that WMO of light ozonation degree containing dispersed mechanical and tarry products proved to be efficient flotation reagents for flotation of coking coal.

WMO purified from mechanical and tarry products may be used as additional hydrocarbon resources to obtain new versatile base oils [2].

Resins isolated from ozone-treated WMO may be used to manufacture bitumen, varieties of oil carbon, natural depressors, pipeline insulation, etc. [5, 6].

TABLE 6

Elemental analysis of powdered residue of WMO, mass %

C	O	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Fe	Ni	Cu	Zn
35.3	23.9	0.7	2.4	5.6	0.3	1.5	0.5	0.5	6.7	0.1	0.2	20.9	0.2	0.2	0.8

The components of the solid powdered residue from WMO are also valuable material resources due to the presence of organic and mineral components, the absence of toxic impurities, so they may find application as initial materials or additives into basic mixtures for the production of asphalt- and cement-concrete materials for technical purposes [5, 6].

CONCLUSION

The major features of WMO ozonation and the regularities of transformations in the structural fragments of their component were established:

1) ozonolytic treatment of WMO for the purpose of separating mechanical and tarry products is more efficient with the specific consumption of ozone ~11 g/kg;

2) reactions with ozone are mainly participated by unsaturated compounds and alkyl substituents of aromatic structures, which promotes an increase in the content of compounds with *n*- and cycloalkyl hydrocarbon framework in WMO;

3) ozonation of oil products promotes the appearance of oxygen-containing compounds with different functional groups: aldehydes, acids, linear and cyclic ethers, which add to the composition of tarry products;

4) the fragment composition of WMO after ozonation and separation of mechanical and tarry products becomes close to that of the base mineral oil;

5) the products of WMO ozonation, namely purified oils, resins, mineral deposits, may be again used as initial raw material or components in petrochemical and other branches of industry.

Acknowledgements

The authors express gratitude to the employees of the FRC CCC SB RAS A. V. Shilyaev, Yu. A. Kharlampenkova, R. I. Furega, S. A. Sozinov, S. Yu. Lyrshchikov, L. M. Khitsova for assistance in the work and in carrying out physicochemical analyses.

REFERENCES

- 1 Review of the Russian market of lubricating materials, 2015 [Electronic resource]. URL: [https://www.ey.com/Publication/vwLUAssets/EY-russian-lubricants-market-rus/\\$FILE/EY-russian-lubricants-market-rus.pdf](https://www.ey.com/Publication/vwLUAssets/EY-russian-lubricants-market-rus/$FILE/EY-russian-lubricants-market-rus.pdf) (Accessed: 30.10.2018).
- 2 Pawlak Z., Urbaniak W., Kaldonski T., Styp-Rekowski M., *Ecological Engineering*. 2010. Vol. 36. P. 1761–1764.
- 3 Ucar S., Özkan A. R., Karagöz S., *Journal of Analytical and Applied Pyrolysis*. 2016. Vol. 119. P. 233–241.
- 4 Fernandes Sara R. M., Silva Hugo M. R. D., Oliveira Joel R. M., *Construction and Building Materials*. 2018. Vol. 160. P. 714–724.
- 5 Pawlak Z., Urbaniak W., Kaldonski T., Styp-Rekowski M., *Ecological Engineering*. 2010. Vol. 36. P. 1761–1764.
- 6 Jafari A. J., Hassanpour M., Resources, *Conservation and Recycling*. 2015. Vol. 103. P. 179–191.
- 7 Zaikov G. E., Rakovsky S. K. Ozonation of Organic and Polymer Compounds. Shawbury, Shrewsbury, Shropshire: Smithers Rapra. 2009. 412 p.
- 8 Likhterova N. M., Lunin V. V., Torkhovskiy V. N., Sazonov D. S., Vasilyeva E. S., Kirillova O. I., *Khimiya i Tekhnologiya Topliv i Masel*. 2006. No. 4. P. 18–21.
- 9 Patrakov Yu. F., Semenova S. SA., Klein M. S., *Koks i Khimiya*. 2018. No. 8. P. 24–28.
- 10 Pretsch E., Bühlmann P., Affolter C. Structure Determination of Organic Compounds – Tables of Spectral Data, Translated from English by B. N. Tarasevich, Mir, Binom, 2006. 438 p.
- 11 Sadykov B. R., Starikov V. P., Sadykov R. Kh., Kalabin G. A., *Neftekhimiya*. 2012. V. 52. No. 1. P. 25–30.
- 12 Patrakov Yu. F., Semenova S. A., Klein M. S., Avid B., *Koks i Khimiya*, 2018. No. 9. P. 2–7.
- 13 Semenova S. A., Patrakov Yu. F., Klein M. S., *Khimiya Tverdogo Topliva*. 2018. No. 4. P. 41–46.