Changes in the Thermal Stability of Mineral Motor Oils After its Using in Diesel Engine

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***Abstract* — It is studied the process of thermal stability of the fresh and waste mineral motor oils for the diesel engine. Based on the results of the research it's been established that the chemical composition of mineral motor oisl after their exploitation depends primarily on the type of engine and its service conditions. It is shown that thermal stability of the studied petroleum motor oils under the same conditions is not the same, due to a change in the chemical composition and the uneven wear and tear additive package.**

Keywords: waste motor oils, thermogram, mass loss, thermolisys, chemical composition

The motor oil is important element in the internal combustion engine construction, because it has considerable influence on the reliability of its work. The ability of oil to counteract thermal, mechanical and chemical effects is a guarantee of a long duration of the engine operating. The main factor affects the motor oil source is a temperature on the friction surface and heated parts. Accordingly, the thermal stability of the oil is primary indicator at its selection for engines with different degrees of capacity. At the same time temperature has influence on oxidation processes and processes of additives destruction and fundamental basis of the oil[1,2]. The temperature method of testing lubricating layers helps to get the data about the thermal stability at the friction of any lubricants.

I. The starting materials

For investigation we selected M-10DM mineral motor oil. The samples before using in the augmented diesel engine and after finishing standard service life (approximately 350 motor hours) of oil were studied. For virgin M-10DM motor oil, it was found: kinematic viscosity ν_{50} = 60,13 mm^2/s, ν_{100}= 11,40 mm^2/s; viscosity index (VI) 95; density 889 kg/m^3; acid number (AN) 1,30 mg KOH/g; base number (BN) 5,83 mg KOH/g; flash point 230 °C; freezing point -20 °C.

For used M-10DM motor oil it was found: kinematic viscosity ν_{50} = 51,65 mm^2/s, ν_{100}= 10,22 mm^2/s; viscosity index (VI) 88; density 884 kg/m^3; acid number (AN) 2,71 mg KOH/g; base number (BN) is absent; flash point 215 °C; freezing point -19 °C.

II. The studying of mineral motor oils thermal stability

Group hydrocarbon composition was studied by a 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[3].

The widespread thermal analysis methods are thermogravimetric and differential-thermal.

One of the varieties of the differential-thermal method is derivatographic analysis. The fundamental principle of it is a comparison of thermal properties of testing substance sample and thermally-inert substance of the ethanol. Derivatographic method allows combining derivatographic thermal analysis and thermogravimetric analysis, what enables to determine thermal stability and thermal effect in compound simultaneously.

Investigation of thermal stability of oil samples was performed on a derivatograph Q-1500D (Paulik-Paulik-Erdey system) with the registration of the analytical signal of mass loss and heat effects using a computer[4]. The samples were analyzed under a dynamic mode with a heating rate of 10°/min in the air. The weight of the samples was 100 mg. The reference substance was aluminum oxide.

III. Results and Discussion

If we analyze the changes in the group composition (Table 1), we observe the decrease in the amount of paraffin-naphthenic hydrocarbons and increase of monocyclic aromatics and tarry asphaltene substances for the used oil. It means that during operation the destruction of paraffin hydrocarbons, dehydration of naphthenic hydrocarbons and condensation of aromatic hydrocarbons take place leading to the formation of tarry asphaltene substances.

TABLE 1

GROUP COMPOSITION OF M-10DM OIL

Group	Virgin oil	Used oil
Paraffin-naphthenic Hydrocarbons	75,2	71,0
Aromatic monocyclic hydrocarbons	5,6	10,7
Aromatic bicyclic hydrocarbons	15,7	14,2
Aromatic polycyclic hydrocarbons	1,9	1,2
Tarry asphatene substancs	1,6	2,9

To establish the change in thermal stability of M-10DM we carried out derivatographic investigations before and after engine operation. According to the results of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) of the virgin and used oils the thermolysis takes place over two or three stages, respectively (Figs. 1-2).

Thermolysis of the virgin oil (Fig. 1) takes place over three stages. The first stage, when the sample looses the

main mass (Dm = 87.20 %) is within the temperature range of 20–390 °C. This stage is accompanied by the appearance of intense exothermal effect on DTA curve with the maximum at 347 °C and corresponds to a thermooxidative destruction of hydrocarbons and their partial combustion. The second stage is within the range of 390–577 °C. It is accompanied by the appearance of the next exothermal effect on DTA curve with the maximum at 494 °C and corresponds to the combustion of pyrolytic residue (Dm = 11.45 %). At the third stage of thermolysis within 577-725 °C the combustion of carbonized residue takes place. This process is accompanied by a slight mass loss (Dm = 1.35 %) and appearance of the third exothermal effect on DTA curve with the maximum at 640 °C.

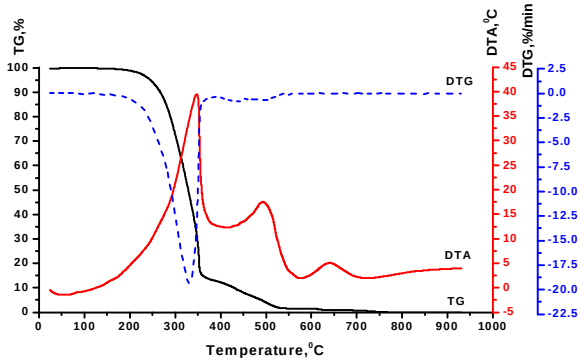

Fig.1. Thermogram of the virgin oil

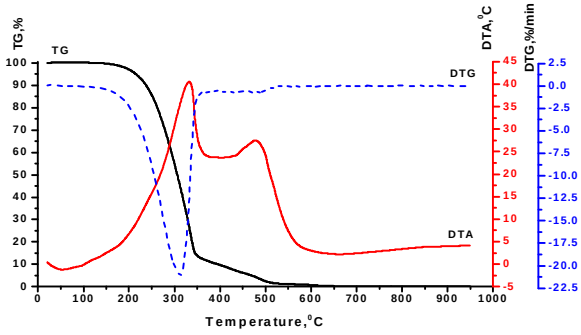

Fig.2. Thermogram of the used oil

Thermolysis of the used oil (Fig. 2) takes place over two stages. The first stage corresponds to the thermooxidative destruction of the sample and partial combustion of destruction products (D*m* = 89.47 %, temperature range 20–387 °C). The first exothermal effect appears on DTA curve with the maximum at 331 °C. At the second stage within 387–650 °C the complete combustion of pyrolytic residue takes place (D*m* = 10.53 %) and the second exothermal effect has the maximum at 479 °C.

It should be noted that the used oil has a lower thermal stability compared with that of the virgin oil. The reason is the decrease in additives amount. While heating the used oil loses its mass more intensive than the virgin oil (Fig. 4) and maxima of its exothermal effects are shifted to the area of lower temperatures (Fig. 5). The combustion of pyrolytic residue takes place over one stage for the used oil and is accompanied by the appearance of only one exothermal effect.

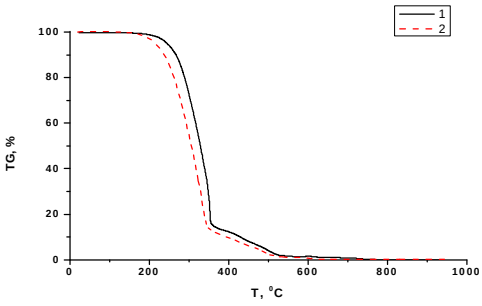

Fig.3. TG curves of M-10DM: virgin oil (1); used oil (2)

The combustion of pyrolytic residue of the virgin oil takes place over two stages within wider temperature range (390–725 °C). Two exothermal effects appear on DTA curve.

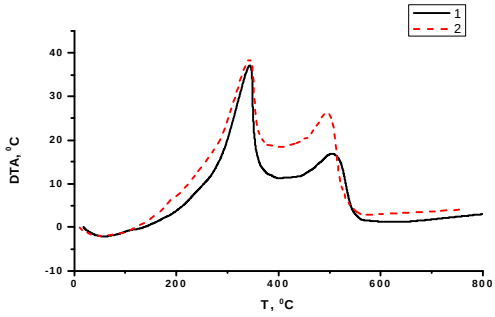

Fig.4. DTA curves of M-10DM: virgin oil (1); used oil (2)

Conclusion

It has been studied the thermal stability of fresh and waste mineral motor oil M-10DM for diesel engines. With the help of derivatographic research, it has been established that waste oil M-10DM differs in lower thermal resistance in comparison to the fresh oil. The waste mineral oil is characterized by lower thermal stability in comparison to the fresh oil, what is caused by the change of chemical composition and wear and tear the additives package while operating.

References

[1] M.M. Runda, B.Y. Koval'skyy, N.N. Malysheva, Y.A .Shumovskyy, “Metodyka predvarytel'noho vybora motornykh masel”, Vestnyk YrHTU, Khymyya y metallurhyya, Yzdatel'stvo YrHTU, vol. 8(67), pp. 130-135, 2012.

[2] S.V. Boichhenko, “Rational using of hydrocarbon fuels”, Kiev, NAU, 216 p., 2001.

[3] V.H. Shram, B.Y. Koval'skyy, N.N. Malysheva, E.H. Kravtsova, “Yssledovanye protsesov tempera-turnoy destruktsyy motornykh masel razlychnykh bazovykh osnov”, Vestnyk YrHTU, Khymyya y metallurhyya, Yzdatel'stvo YrHTU, vol. 1(72), pp. 117-120, 2013.

[4] V. Y. Ysahulyants, H. M. Ehorova, ”Khymyya nefty”, Moscow, Khymyya, 517 p, 1965

[5] F.Paulik, J. Paulik, and L Erdey, "Derivatography: A complex method in thermal analysis." Talanta 13.10, pp.1405-1430, 1966.