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A LABORATORY STUDY OF THE ANTIOXIDATION EFFECTIVENESS OF MOTOR-OIL ADDITIVES

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A large part of the papers dealing with the effect of additives which increase the stability of mineral oils with respect to oxidation pertain to turbine and transformer oils with the scope of these investigations being confined to relatively low temperatures — 100 - 140° C.

Recently, antioxidation additives to motor oils have also acquired broad application, but there is very little data pertaining to their effectiveness at the temperatures characteristic of the operating conditions of an engine. We are not always able to determine the effect of an additive on the extent of oxidation of an oil from this data, since at high temperatures the oxidation processes in the oil are extremely complicated and proceed in parallel with polymerization and condensation reactions between the products of the oxidation, and also with reactions involving the cleavage and volatilization (loss) of these products.

The criterion often applied to determine the extent of oxidation

of motor oils is not the amount of oxygen entering into the reaction, but the amount of certain products which are formed as a result of the oxidation and which are of practical importance under operating conditions. Thus, for example, in the thermal-oxidation stability method (GOST 9352-60) the criterion for the rate of oxidation has been taken as the time necessary to obtain a "residue", consisting of 50% lacquer (a product of the oxidation polymerization and condensation), which is not soluble in light gasoline, and 50% soluble lacquer. The oxidation proceeds at a temperature of 250° under conditions of free diffusion of atmospheric oxygen (oxidizing agent) and free vaporization of volatile oxidation products as well as of the light fractions of the oil itself. According to the method developed by NAMI, (State All-Union "Order of The Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute), oxidation is carried on for 50 hrs at 200° under conditions of free access of the oxidizing agent, atmospheric oxygen, but preventing the free vaporization of the oil and the products of its oxidation. The criteria for appraising the extent of oxidation are the increase in the oil viscosity and the amount of sediment (the oxidation products) not soluble in light gasoline. Therefore, the lacquer in the GOST 9352-60 method and the sediment in the NAMI method are in this sense identical concepts.

The criterion for the extent of oxidation of the oil proposed by the Azerbaydzhan Scientific Research Institute for Oil Refining is the amount of absorbed oxygen. The oxidation is carried out in a closed system at 175° with oxygen at atmospheric pressure. But the oil does not undergo any pronounced change, and the rate of oxidation is evaluated on the basis of the time necessary for the absorption of

0.8 ml of O_2 by 1 g of oil.

In this paper the authors have attempted to compare and interpret results obtained by these three methods in an effort to ascertain the antioxidation effectiveness of motor-oil additives.

The experiments using the ASRIOR method were carried out under a different regime: a temperature of 200° and an absorption of about 5 ml of oxygen by 1 g of oil.

Data from investigations of 6 oil samples are presented in Figs. 1 to 3: 1) DS-11 base oil (NKZ); 2) the same oil with 3% cyatim-339 additive; 3) the same with 3% cyatim-339 additive (alkaline) containing an excess of barium (BaO, $BaCO_3$); 4) the same with bartiol import additive (3%), which is barium dialkyldithiophosphate; 5) the same with bartiol additive (alkaline) containing an excess of barium; 6) the same with gintset additive, which is a mixture of zinc dialkyldithiophosphate and barium and calcium sulfonates.

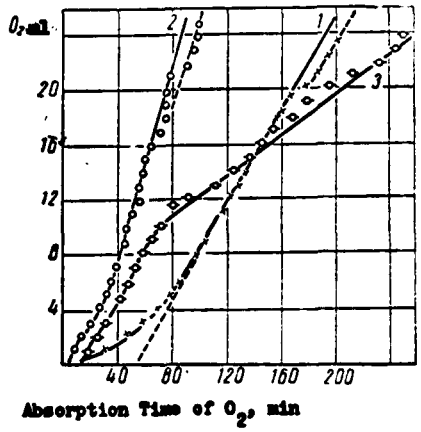

Fig. 1. Absorption of oxygen by oil at 200°. ASRIOR instrument, 5 ml of oil. 1) DS-11 (NKZ) without additive; 2) the same with 3% cyatim-339 additive; 3) the same with 3% cyatim-339 alkaline additive.

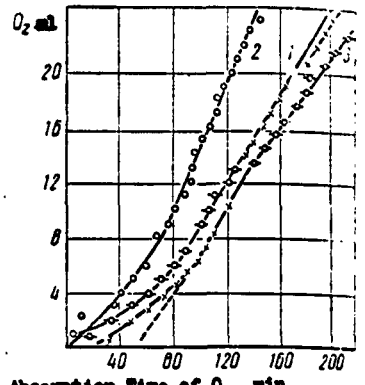

Fig. 2. Absorption of oxygen by oil at 200°. ASRIOR instrument, 5 ml of oil. 1) DS-11 (NKZ) without additive; 2) the same with 3% bartiol additive; 3) the same with 3% bartiol alkaline additive.

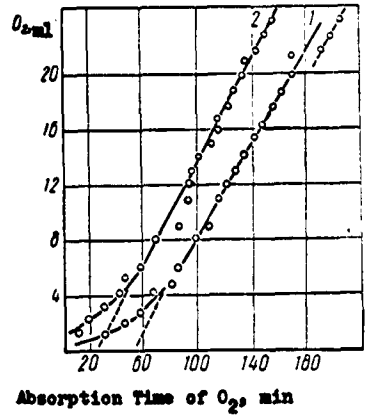

Fig. 3. Absorption of oxygen by oil at 200°. ASRIOR instrument, 5 ml of oil. 1) DS-11 (NKZ) without additive; 2) the same with 5% gintset additive.

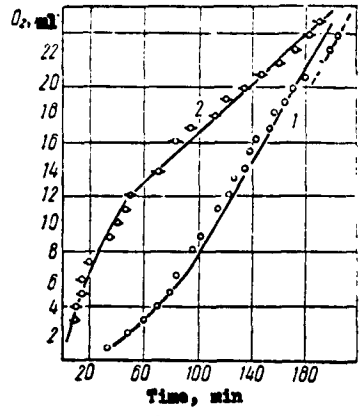

Fig. 4. Absorption of oxygen by oil at 200°. ASRIOR insrument, 5 g of oil. 1) DS-11 (NKZ) oil without additive; 2) SAE-30 oil (with alkaline sulfonate additive).

The results of experiments on the absorption of oxygen by 5 g of the first three samples in the ASRIOR instrument at 200° are plotted in Fig. 1. Similar data are presented for the fourth and fifth samples in Fig. 2 and for the sixth sample in Fig. 3. The curve for the base oil, the first sample, is also given in Figs. 2 and 3 for the purpose of graphic comparison.

The absorption curves do not indicate the presence of any real induction period characteristic of the oxidation of oil at lower temperatures. In the first period (60-70 min) the absorption proceeds at a variable rate, after which the curves straighten out. The absorption rate of the oxygen was calculated on the basis of the rectilinear portions of the curves. The values thus obtained give some idea of the rate of the oxidation reaction for more pronounced oxidation.

In the data presented in Figs. 1-3 it is noteworthy that the cyatim-339 (curve 2 in Fig. 1), bartiol (curve 2 in Fig. 2), and gintset

(curve 2 in Fig. 3) additives do not decrease, but rather increase the rate of absorption of the oxygen, in spite of the fact that the bartiol additive is barium dithiophosphate in pure form, while the gintset additive contains zinc dithiophosphate in its composition. On the other hand, in the presence of excess alkalinity the cyatim-339 and bartiol additives significantly decelerate the absorption of oxygen (curves 2 in Fig. 1 and 3 in Fig. 2). The effect of this alkalinity on the rate of oxygen absorption is also common to the other additives; this is illustrated in Fig. 4 for SAE-30 oil (curve 2 in Fig. 4).

In the table we have compared the results of investigations of the value of the thermal-oxidation stability in minutes obtained by the GOST 9352-60 method and the percentage of lacquer obtained during this time. These studies were conducted on 6 oil samples on the DK-2 instrument at 200° for a period of 50 hrs using the NAMI method. In the same place we have listed the values of the oxygen absorption rate (curves 1, 2, and 3) calculated in ml of O_2/min·g of oil·100.

TABLE 1

Results of Oxidation of DS-11 Oil with Additives in a DK-2 Instrument at 200° and by the Method of Thermal-Oxidation Stability at 250°.

Sample Number	Additive	Oxidation temperature of 200°				Oxidation temperature of 250°	
		DK-2			ASRIOR		
		$\Delta\nu_{100}$, cs (with sediment)	$\Delta\nu_{100}$, cs (without sediment)	Sediment %	O_2, ml/min·g·10^3	TOS, min	Lacquer %
	Without additive	10,3	3,8	4,0	3,19	33	13
	Cyatim-339 (3%)	22,5	5,34	8,3	6,67	55	11
	Cyatim-339 alkaline (13%)	12,5	7,30	2,0	1,48	38	12
	Bartiol (3%)	21,4	2,9	8,5	5,0	110	8
	Bartiol alkaline (3%)	12,4	5,5	4,0	2,27	85	9,5
	Gintset (5%)	12,65	2,55	6,5	4,0	74	10

From the data listed in the table concerning the increase in viscosity during oxidation by the NAMI method, $\Delta\nu_{100}$ cs (with sediment), it follows that all 5 additives are oxidants at 200°. On the basis of this criterion excess alkalinity in the additive material lessens its oxidant effect. If we judge on the basis of sedimentation (NAMI method), it follows that the cyatim-339, bartiol, and gintset additives are oxidants. Excess alkalinity in the cyatim-339 additive makes it an antioxident, while alkalinity in the bartiol additive destroys its oxidant property. Therefore, the evaluation of the additives by the NAMI method and on the basis of oxygen absorption in the ASRIOR instrument at 200° is practically the same.

The results obtained with the thermal-oxidation stability method at 250° give a contradictory evaluation of these additives. All the additives tested were evaluated as antioxidants both on the basis of the formation time of a lacquer residue of prescribed composition (in minutes), and on the basis of the amount of lacquer obtained (in %). Excess alkalinity does not increase the antioxidant effectiveness of the additive, but, instead, decreases it.

Data concerning the magnitude of the increase in the viscosity $\Delta\nu_{100}$ cs (without sediment) are presented in the table. This value was obtained by determining the viscosity of the oxidized oil after the removal of the sediment and represents the increase in viscosity due to the accumulation of gums formed in the oil during its oxidation. With further oxidation these gums may be converted into more compact compounds and are separated out of the oil in the form of a sediment. It is noteworthy that the amount of gum increases with the alkalinity of the additive with a concomitant decrease in the sediment, which is apparent from samples 2-3 and 4-5. In the experiments at 250° an

increase in the alkalinity led to an increase in the lacquer and a decrease in its time of formation, which is obviously due to the accumulation of gums.

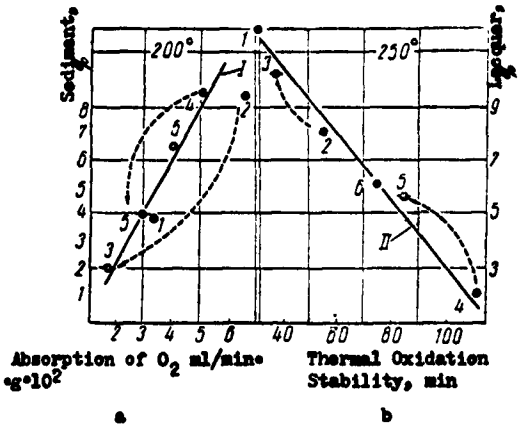

Fig. 5. Amount of sediment as a function of oxygen absorption rate (a); amount of lacquer (in %) as a function of thermal-oxidation stability in minutes (b). Note: The point numbers correspond to the oil samples listed in the table.

Figure 5 graphically illustrates this contradictory appraisal of the data obtained by the method of thermal-oxidation stability at 250°, and by the NAMI method and the method of oxygen absorption in the ASRIOR instrument at 200°. Curve I in Fig. 5a shows the dependence of sedimention (by the NAMI method) on the oxygen absorption rate, while curve II shows the dependence of the amount of lacquer (for prescribed composition of lacquer residue) on its time of formation. For both curves the arrows indicate the effect of excess alkalinity in the additive on the antioxidation stability of the oil. Curve I shows that excess alkalinity in the cyatim-339 additive (points 2 and 3) and in the bartiol additive (points 4 and 5) increases the stability of the oil at 200°, while curve II shows a decrease in stability.

The bartiol and gintset additives which contain the thiophosphate group behaved as oxidants in the experiments at 200° not only with respect to sedimentation, but also with respect to the oxygen absorption rate. This occurs as a result of the fact that the anti-oxidation effectiveness of thiophosphate additives, as that of many other antioxidants, decreases with an increase in temperature, and, when a certain temperature has been reached, they become oxidants. However, as is apparent from Fig. 5 (thermal-oxidation stability method), these same additives behaved as extremely effective anti-oxidants.

This apparent contradiction is explained by the fact that under conditions of free vaporization a number of products of the oxidation of the oil, which are capable of undergoing condensation and polymerization, are volatilized. These same products under conditions which hinder vaporization may be separated out in the form of a sediment which is not soluble in light gasoline. The presence of an additive which acts as an oxidant at a given temperature increases the formation of these volatile oxidation products.

All of these theories concerning the effectiveness of antioxidant additives, which have been put forth on the basis of the experimental data presented herein may serve as a working hypothesis for further investigations of oils with additives. Final and comprehensive data concerning the antioxidant and oxidant effects of motor-oil additives may be obtained only by methods based on absorption of oxygen at high temperatures. The development of such methods is a problem which is inseparable from the problem of developing antioxidant additives.

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