measures is the establishment of an optimal concentration of FSII in fuel (in most cases 0.1%), with due regard for the design features and operating conditions of the flight vehicle.

LITERATURE CITED

1. V. T. Vasilenko and Zh. S. Chernenko, Influence of Operating Factors on Aircraft Fuel Systems [in Russian], Mashinostroenie, Moscow (1986), p. 41.
2. B. G. Bedrik, S. I. Uspenskii, and V. N. Golubushkin, Khim. Tekhnol. Topl. Masel, No. 7, 22-23 (1983).
3. B. G. Bedrik, T. F. Radkevich, and V. N. Golubushkin, in: Summaries of Papers from 5th All-Union Scientific-Technical Conference, held in Kiev on October 8-10, 1981 [in Russian], Kiev (1981), p. 79.
4. A. A. Bratkov (editor), Chemmotology of Rocket and Jet Fuels [in Russian], Khimiya, Moscow (1987).
5. B. A. Énglin, Application of Liquid Fuels at Low Temperatures [in Russian], Khimiya, Moscow (1980).
6. A. S. Polyakov, K. V. Rybakov, and N. V. Tkham, Tr. Kiev. Inst. Ing. Grazhd. Aviats., pp. 83-84 (1979).

CATALYTIC EFFECT OF COPPER ON OXIDATION

OF PETROLEUM OIL WITH ADDITVES

A. B. Vipper, G. M. Balak,   UDC 621.892.86:542.943.7:546.56-121
N. A. Ponomarenko, and L. L. Kalinin

One of the most important properties of motor oils in terms of service is their oxidation resistance. The serviceability of motor oils and the oil drain periods in internal combustion engines are determined largely by the oil oxidation resistance. Metals such as iron, aluminum, and copper — metals from which the engine parts are manufactured — are major factors in motor oil oxidation and aging. Of the metals, copper is the most active oxidation catalyst. In heterogeneous catalysis, the metal surface has a catalytic effect because of chemisorption of oxygen on the surface [1]; in homogeneous catalysis, oil-soluble metal salts have a catalytic effect as a consequence of the formation of free radicals [2]. Various types of additives, such as inhibitors, deactivators, and passivators, are incorporated into the oil in order to reduce the catalytic effect of metals.

The work reported here was aimed at a comparison of the efficiencies of additives belonging to the classes of oxidation inhibitors and copper passivators. For this comparison it was necessary to determine the rate of accumulation of oil-soluble copper compounds in the oil during oxidation in the presence of copper strips or wire coils, to investigate the oxidizability of the oil at moderate and elevated temperatures with and without copper, and to establish the relation between the content of copper in the oil and the oxidizability of the oil in the presence of different types of additives.

As objects of investigation we selected M-11 motor oil, the antioxidant DF-11 (zinc dialkyldithiophosphate) at a concentration of 1%, and the copper passivator benzotriazole at a concentration of 0.1%. The oil samples were oxidized at 100° and 180°C (tests at temperatures above 180°C may result in very severe thickening of the oil). In the tests at 100°C, a 70-g oil sample was held 200 h in a glass flask with a copper strip (49 × 19 × 2.5 mm), positioned at a 45° angle.

In the tests at 180°C, a 25-g oil sample was tested in a unit described in [3], consisting of a heater section and an air feed system, the latter including a laboratory air trap, a surge tank, and a system of differential manometers. The heater section consisted of a thermostated bath with four wells holding four glass reactor flasks, each of which had a
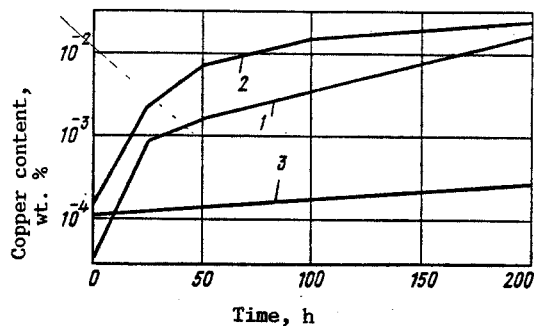
Fig. 1. Change in copper content in M-11 oil during oxidation at 100°C: 1) without additive; 2) with 1% DF-11; 3) with 0.1% benzotriazole.
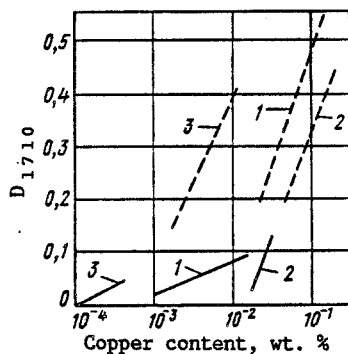

Fig. 2. Optical density D_{1710} of M-11 oil as a function of copper content in the process of oxidation. Solid lines are for tests at 100°C with copper strip; dashed lines are for tests at 180°C with copper coil. Other notations same as in Fig. 1.

TABLE 1

M-11 oil	Oxidation time, h	Optical density D_{1710}
With copper strip		
Without additive	200	0,035
Without copper strip		
Without additive	50	0,028
	100	0,047
	200	0,097
With 0.1% benzotri-azole	50	0,010
	200	0,036
With 1% DF-11	200	0,048

capillary for injection of the air into the oil sample (capillary diameter 0.7 mm, distance from bottom end of capillary to reactor flask bottom 5 mm). As a catalyst we used a copper coil (coil diameter 20 mm, coil length 17 mm, wire diameter 1.8 mm). The air input rate was 200 ml/min, and the oxidation test period was 15 h. Oil samples were taken at 5 and 10 h and at the end of the test.

Oxidation products containing the carbonyl group were characterized by the intensity of the IR absorption band with a maximum at 1710 cm^{-1} [4-6] determined on a Specord 751R spectrophotometer. The content of copper in the oil was determined by atomic absorption on a Perkin-Elmer Model 303 spectrometer (analytical line of copper 324.8 nm [7]).
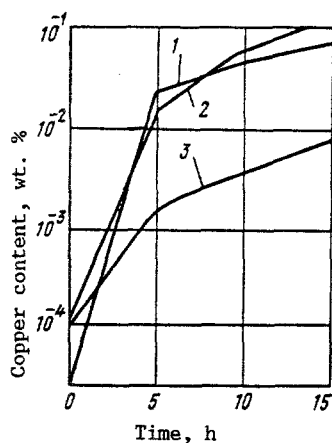
Fig. 3. Changes in content of copper in M-11 oil during oxidation at 180°C. Notations same as in Fig. 1.

TABLE 2

M-11 oil	Opt. dens. D_{1710} of oil after oxidat. at 180°C for indicated period		
	5 h	10 h	15 h
Without copper coil			
Without additive	0,091	0,188	0,241/0,256
With 1% DF-11	0,110	0,179	0,215/0,217
With 0.1% benzotriazole	0,058	0,128	0,178/0,194
With copper coil			
Without additive	0,242	0,372	0,506/0,507
With 1% DF-11	0,043	0,265	0,403/0,481
With 0.1% benzotriazole	0,172	0,263	0,409/0,376

Note. First value is for sample 1, second value for sample 2.

The results obtained in oxidation tests on the M-11 oil at 100°C are presented in Figs. 1 and 2 and Table 1. As can be seen from Fig. 1, the oil accumulates copper rapidly, particularly in the first 25 h of oxidation, after which the accumulation rate becomes practically constant. Benzotriazole gives a very marked reduction of the dissolution of copper and its entry into the oil. In the oil with the DF-17 additive, the copper accumulation is slightly greater than in the oil without the additive; only after 200 h of oxidation do the copper contents in these two samples become practically equal. Both the benzotriazole and the DF-11 retard the accumulation of carbonyl-containing oxidation products in the oil, bringing the accumulation down to the level observed in the oxidation test on oil without a copper strip (Table 1).

The quantity of carbonyl-containing oxidation products accumulated in the oil is linearly related to the copper content (Fig. 2). The DF-11, in contrast to the benzotriazole, prevents the participation of copper in the catalytic oxidation of the oil. Because of this, an equal quantity of oxidation products is formed with a larger quantity of copper in the oil in the case of the DF-11, in comparison with the oil without additive. In the oil with the benzotriazole, the ratio between the quantities of oxidation products and copper is higher than in the oil without additive.

Thus, the DF-11 and the benzotriazole differ substantially in the character of their influence on the copper-catalyzed oxidation of oil: Benzotriazole retards the accumulation of copper in the oil, whereas the DF-11 additive accelerates the accumulation of copper. Along with this, however, it suppresses much of the catalytic effect of copper on the oil oxidation. In terms of overall effect of the additive on the oxidation of M-11 oil in the presence of the copper strip catalyst, the two additives are practically identical (see Table 1).

The results obtained in oxidation tests on the oil at an elevated temperature (180°C) are presented in Figs. 2 and 3 and Table 2. The data shown in Fig. 3 indicate rapid accumulation of copper in the oil (particularly in the first 5 h of oxidation) under conditions of high temperature and air bubbling through the oil; subsequently, the rate of entry of copper into the oil drops off gradually. The specific effects of these two additives on the copper accumulation process in the tests at 100°C are still observed at 180°C: In the oil with the benzotriazole, the dissolution of copper is considerably slower than without the additive; in the oil with the DF-11, the quantity of copper accumulated is practically the same as without the additive. The influence of benzotriazole on the rate of copper accumulation in the oil is particularly significant in the first 5 h of oxidation. In this stage of the test, the rate of copper entry into the oil is considerably lower than in the subsequent stages; in the period of the test from 5 to 15 h, the rate of copper accumulation is practically the same for all of the oil samples.

The copper accumulated in the oil produces a considerable acceleration of the oxidation process for the straight oil and also for the oils with additives (Table 2). As a consequence, the amount of carbonyl-containing oxidation products accumulated in the oil in the tests with copper catalyst is approximately twice the amount accumulated in the tests without catalyst. In the absence of copper, the DF-11 and benzotriazole have smaller effects on the rate of oxidation product accumulation in the oil in comparison with the tests in which the copper coil is present. In the copper-catalyzed tests, the DF-11 is especially effective in the first 5 h of oxidation, after which the rate of accumulation of oxidation products increases sharply, apparently indicating exhaustion of the DF-11 at the end of this first stage of the test.

The quantity of copper accumulated in the oil at 180°C, the same as at 100°C, is linearly related to the amount of carbonyl-containing oxidation products accumulated (Fig. 2). The ratio of these quantities is different for each of the oil test samples. The same as in the tests at 100°C, the DF-11 additive in the tests at 180°C is effective in preventing the catalytic action of considerable quantities of copper in terms of oil oxidation. In the presence of benzotriazole, the copper accumulated in the oil has a greater effect in catalyzing the oil oxidation process in comparison with the test on the oil without benzotriazole (Fig. 2).

Thus, a linear relationship exists between the content of copper in the oil and the quantity of carbonyl-containing oxidation products accumulated in the oil. Under the more severe conditions of experiment, the slopes of the lines characterizing this relationship are different from those for the less severe test conditions.

The conditions we selected for our experiments have enabled us to differentiate additives very clearly with respect to their influence on the catalytic effect of copper in the oil oxidation process, and to determine additive exhaustion in this process. The passivating effect of benzotriazole is related solely to its influence on the rate of accumulation of copper (and its oil-soluble compounds) in the oil; the DF-11 additive accelerates this process slightly, at the same time hindering the catalytic effect of copper present in the oil on the process of oxidation product accumulation in the oil.

LITERATURE CITED

1. N. M. Émanuel, E. T. Denisov, and Z. K. Maizus, Liquid-Phase Oxidation of Hydrocarbons, Plenum Press, New York (1967).
2. R.A.Lipshtein and M. I. Shakhnovich, Transformer Oils [in Russian], Énergiya, Moscow (1983).
3. A. V. Kozhekin, V. N. Bauman, and A. N. Ershova, Khim. Tekhnol. Topl. Masel, No. 7, 20-22 (1983).
4. A. B. Vipper and V. A. Tarasov, Khim. Tekhnol. Topl. Masel, No. 9, 48-52 (1969).
5. G. T. Vigant, G. I. Krylova, N. P. Yurchenko, et al., Khim. Tekhnol. Topl. Masel, No. 4, 55-57 (1978).
6. A. A. Gundyrev, L. P. Kazakova, and I. G. Fuks, IR Spectroscopy of Paraffin Waxes and Greases [in Russian], MING im. I. M. Gubkina, Moscow (1986).
7. G. M. Balak, L. L. Kalinin, and O. V. Kovaleva, Khim. Tekhnol. Topl. Masel, No. 1, 32-34 (1987).