COOPERATIVE EFFECT OF ZINC DITHIOPHOSPHATE AND COPPER PASSIVATORS

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UDC 621.892.86:542.943.7:546.56-121

Studies of the catalytic effect of copper on the oxidation of motor oils have shown that zinc dialkyldithiophosphate promotes the process of copper build-up or accumulation in oil, which effectively inhibits or obstructs the catalytic effect of oil-soluble copper salts on the formation of oxidation products. The effect of benzotriazole on the copper-catalyzed oxidation of oil is due to its ability to decrease sharply the rate of copper build-up in oil [1]. In light of these results, it was of interest to us to check the efficacy of the simultaneous or cooperative activity of zinc dithiophosphate and a copper passivator, since in the case that each of these specific additive effects on the accumulation of copper salts and on the feasibility of homogeneous catalysis is retained, the serviceability of the antioxidant additive may be significantly enhanced.

Since benzotriazole (BTA) is sparingly soluble (less than 0.1 weight %) in oil, we also examined additive A, which consists of a benzotriazole derivative which has excellent solubility in motor oil. The zinc dialkyldithiophosphate derivative DF-11 was used as the antioxidant additive. The studies were carried out in M-11 oil using the high-temperature oxidation method [1], with copper coil acting as the catalyst. The concentration of copper in the oils studied was determined by atomic absorption spectroscopy; the composition of the oxidation products was monitored using IR spectroscopy on a Perkin-Elmer spectrophotometer (model 325, 0.1 mm-thick KBr cuvette).

The relationship between the degree of copper build-up or accumulation (in the form of oil-soluble compounds) in the oil studied and the integrated IR absorption intensity in the 1640-1820 cm^{-1} region is shown in Fig. 1. The latter function was determined by weight from the area under the optical density band envelope $D = f(\nu)$. As can be seen from the graphs in Fig. 1, in all cases the same general relationship is observed, namely, a linear correlation of the two functions stated above; this indicates the critical and fundamental role of homogeneous catalysis. The result for the combination of (antioxidant) additive DF-11 and BTA (with respect to build-up of copper and build-up of oxidation products) was similar to that for benzotriazole alone.

The lowest amount of oxidation products is formed in the oil when the additive DF-11 is used in a mixture with the copper passivator additive A, although the copper concentration in the oil in this case was found to be the same as when a mixture of DF-11 and BTA was used together: in the former case, the value of this function (amount of oxidation products) was 2-times less at the end of the experiment than when M-11 oil was treated with additive DF-11 alone. The superiority of the additive combination DF-11 + A over DF-11 and BTA is also suggested by the data in Table 1.

The ratio of optical densities for the absorption bands with maxima at 1710 and 1770 cm^{-1} was used as an index or criterion of the antioxidant efficiency of additives [2]. It is apparent from this data that to a certain degree the additive BTA suppresses (especially in the initial stages of the experiment) the inherent or intrinsic ability of the additive DF-11 to obstruct the catalytic effect of oil-soluble copper compounds on the build-up of oxidation products in the oil. This property is practically lost in additive A, which explains why the combination of passivator A with additive DF-11 is superior to an additive package containing additive DF-11 and BTA.

In order to elucidate the factors responsible for the different behavior of additives BTA and A on the ability or capacity of zinc dialkyldithiophosphate to obstruct the catalytic

*The spectral measurements were made in the range 250-700 nm, at a scanning rate of 600 nm/min.

I. M. Gubkin Moscow Institute of Oil and Gas. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 24-26, November, 1989.

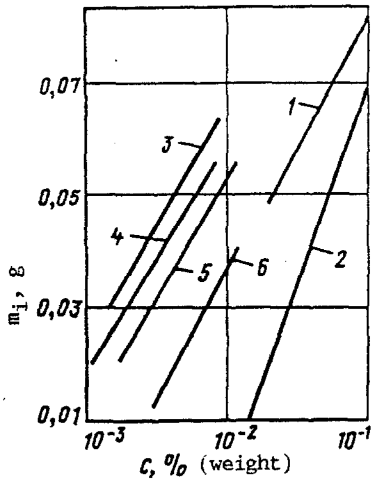

Fig. 1. Relationship between integrated absorption intensity m_i in the 1640-1820 cm^{-1} region and the concentration of copper in M-11 oil: 1) without additive; 2) with 1% DF-11; 3) 0.1% BTA; 4) 0.2% A; 5) 1% DF-11 + 0.1% BTA; 6) 1% DF-11 + 0.2% A.

TABLE 1

M-11 oil	D_{1710}/D_{1770}		
	after 5 h	after 10 h	after 15 h
Without additives	1,85	1,8	1,7
With additive			
1 % DF-11	5,5	2,2	1,9
0,1 % BTA	3,0	2,6	2,3
0,2 % A	3,4	2,7	2,4
1 % DF-11 + 0.1% BTA	3,35	2,65	2,2
1 % DF-11 + 0.2% A	4,85	3,6	2,6

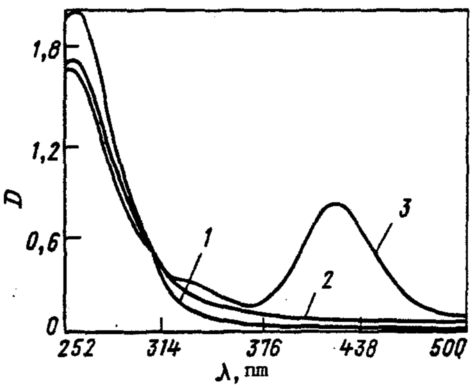

Fig. 2. Absorption spectra (D, optical density; λ, wavelength): 1) additive DF-11; 2) copper naphthenate; 3) reaction products of DF-11 and copper naphthenate.

effect of oil-soluble copper salts on oil oxidation, we also examined the visible (region) absorption spectra of solutions of their (oxidation) products (and mixtures) in isooctane; a Beckman DU-7 spectrophotometer was used.* Copper naphthenate (copper concentration 10.6%) was used as a model for the oil-soluble copper salts which are formed in the oil and which account for homogeneous catalysis. The same ratios of additives used in the oil-oxidation experiments were used in preparing the solutions (for spectrophotometric analysis): DF-11: BTA:A = 10:1:2; DF-11:copper naphthenate = 10:1; BTA: copper naphthenate = 1:1.

*The spectral measurements were made in the range 250-700 nm, at a scanning rate of 600 nm/min.

Treatment of additive DF-11 with copper naphthenate results in the formation of a new compound, as indicated by the appearance of a peak at 419 nm in the absorption spectrum (Fig. 2). We offer the assumption that this compound is the result of an exchange reaction leading to the formation of copper dithiophosphate. Analogous conclusions can be drawn based on the results in [3, 4]. In order to verify this hypothesis, we carried out a similar experiment with additive DF-11 and copper acetate (10:1). Upon reaction of these two substances a new product is also formed (yellow in color), with an absorption peak at 419 nm; this supports the validity of the hypothesis given above. Since the stability constant of copper acetate is higher than that of zinc acetate (2.65 and 1.7, respectively), reaction of additive DF-11 with copper acetate results in the formation of copper dithiophosphate.

Apparently, therefore, zinc dithiophosphate inhibits the catalytic effect of oil-soluble copper salts on oil oxidation by converting these salts into less active compounds, such as, in part, copper dithiophosphate, whose antioxidant activity or efficiency is extremely high. The latter observation is consistent with the results of an earlier study [5], which indicated that with respect to antioxidant properties copper dithiophosphates are far superior to zinc dithiophosphates. Addition of a third component, additive A, to the additive combination DF-11 and copper naphthenate does not lead to any changes in the system. Regardless of the sequence of component addition, reaction of zinc dithiophosphate and copper naphthenate results in the formation of copper dithiophosphate.

A different pattern is observed when the additives BTA, DF-11, and copper naphthenate are combined. Thus, if copper naphthenate and benzotriazole are mixed first, a compound absorbing in the 320-330 nm region in formed. Only after the addition of zinc dithiophosphate to this solution does copper dithiophosphate, which absorbs at 419 nm, begin to form. The amount of the material absorbing at 419 nm subsequently increases with time, while the substance absorbing at 320-330 nm declines. The product formed by reaction of additive BTA and copper naphthenate is apparently less stable than the exchange reaction product, copper dithiophosphate.

The lower antioxidant activity of the additive combination DF-11 + BTA compared to DF-11 and A is due to the ability of benzotriazole to suppress the exchange reaction leading to the formation of copper dithiophosphate, while additive A does not appear to exert any intrinsic effect on the reaction of zinc dithiophosphate with oil-soluble copper salts. When zinc dialkyldithiophosphate and a copper passivator are combined successfully under conditions of copper-catalyzed oxidation of oil, the amounts of oil-soluble copper salts and oxidation products, with characteristic IR absorption in the 1640-1820 cm^{-1} region, in the oil are reduced substantially.

This conclusion makes it possible to increase significantly the effective antioxidant lifetime of zinc dialkyldithiophosphate additives. Since in the presence of oil-soluble copper salts the latter (antioxidant efficiency period) depends upon an exchange reaction which generates copper dithiophosphate (which is superior to zinc dithiophosphate with respect to antioxidant activity), it is advisable to select a combination of zinc dithiophosphate with a copper passivator which does not restrict the exchange reaction.

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