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Abstract

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ANTIOXIDANTS OF THE METAL DIALKYLDITHIOPHOSPHATE TYPE

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In previous work it was shown that certain derivatives of dithiophosphoric acid, namely metal dialkyldithiophosphates, are multifunctional additives for lubricating oils ([1,2]). Additives of this type possess detergent, anticorrosion, and antiwear properties; with appropriate structure they can also serve as depressants and demulsifiers.

In the present work, results are given from a study of metal dialkyldithiophosphates as antioxidants for hydrocarbons in lubricating oils. The comparative antioxidant activity of metal dialkyldithiophosphates of different structures was investigated, and the influence of certain factors on the process of hydrocarbon oxidation in the presence of these additives was shown. For the study, additives were synthesized whose structures are given in Table 1.

Table 1

Structure of additives of the dialkyldithiophosphate salt type

Additive designation	Formula
DF-1	$[(RO)_2PSS]_2Ba,\ R = C_{20} - C_{24}$
DF-2	$[(RO)_2PSS]_2Ba,\ R = C_{16} - C_{20}$
DF-12	$[(CH_3(CH_2)_3CH(C_2H_5)CH_2O)_2PSS]_2Ba$
DF-5	$[(RO)_2PSS]_2Zn,\ R = C_{20} - C_{24}$
DF-8	$[(CH_3(CH_2)_5CH(CH_3)O)_2PSS]_2Zn$
DF-9	$[(CH_3(CH_2)_3CH(C_2H_5)CH_2O)_2PSS]_2Zn$
DF-10	$[CH_3(CH_2)_5CH(CH_3)O]_2PSSZnSSP[OCH_2CH(CH_3)_2]_2$
DF-11	$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2PSSZnSSP[OCH_2CH(CH_3)_2]_2$
–	$[((CH_3)_2CHCH_2O)_2PSS]_2Zn$

Additives DF-1, DF-2, and DF-12 are barium dialkyldithiophosphates; the remaining additives are zinc dialkyldithiophosphates.

To obtain the additives DF-1 and DF-5, high-molecular-weight alcohols obtained by direct oxidation of the paraffin fraction 330–390° were used; to obtain the

Fig. 1. Effect of additive DF-1 on the oxidation of paraffin-naphthenic hydrocarbons. a—paraffin-naphthenic hydrocarbons; b—paraffin-naphthenic hydrocarbons + 1% DF

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additive DF-2, alcohols obtained by oxidation of the paraffin fraction 270–330° were used. The molecular weight of the alcohols corresponded to C_{20}—C_{24} and C_{16}—C_{20}. Additive DF-8 was obtained on the basis of secondary octyl alcohol, *n*-octanol-2, while additives DF-9 and DF-12 were obtained on the basis of primary octyl alcohol, 2-ethylhexanol. Each of the additives DF-10 and DF-11 was obtained from two alcohols and thus contained radicals of different structure.

Fig. 1. Effect of additive DF-1 on the oxidation of paraffin-naphthenic hydrocarbons.
a—paraffin-naphthenic hydrocarbons; *b*—paraffin-naphthenic hydrocarbons + 1% DF

In most experiments, paraffin-naphthenic hydrocarbons isolated by adsorption chromatography from a distillate oil of sulfurous petroleum were subjected to oxidation. Oxidation of the hydrocarbons was determined from the absorption of oxygen by the hydrocarbons in a closed system.

All metal dialkyldithiophosphates slow, to one degree or another, the rate of oxidation of hydrocarbons and thus are typical antioxidants. However, their activity as antioxidants is not the same and depends on the structure of the hydrocarbon radicals and on the nature of the metal. The most active are barium dialkyldithiophosphates containing secondary hydrocarbon radicals.

Figure 1 presents the results of oxidation of paraffin-naphthenic hydrocarbons at various temperatures in the presence of additive DF-1 (high-molecular-weight barium dialkyldithiophosphate).

Antioxidants of the dialkyldithiophosphate type exhibit the greatest activity at temperatures up to 150°. On going to higher temperatures, the action of the antioxidants weakens, apparently owing to their thermal decomposition. The optimum concentrations of the various additives under the adopted oxidation conditions ranged from 0.75 to 2.5%.

The oil from which the unstable paraffin-naphthenic hydrocarbons were isolated also contains monocyclic and bicyclic aromatic hydrocarbons and sulfur compounds. Some aromatic hydrocarbons and, in particular, sulfur compounds of the oil are natural antioxidants with respect to the unstable hydrocarbons of the oil. Therefore the oil itself possesses high stability. The natural inhibitors present in the oil paralyze the action of synthetic antioxidants of the metal di-

alkyldithiophosphate type; under these conditions the latter do not exert any noticeable influence on the oxidation process of the oil itself.

Metals and their oxides (Fe, Cu, CuO) serve as catalysts for the oxidation of hydrocarbons. As was shown, the oil, despite the presence in it

natural inhibitors, in the presence of metals, becomes low-stability.

The catalytic action of metals can be weakened or eliminated by the use of metal dialkyldithiophosphates. Thus, for example, the DF-1 additive in the presence of metals increased the stability of the oil. Dialkyldithiophosphates, as surface-active substances, apparently are adsorbed on the metal surface, thereby exerting an indirect positive influence on the stability of the oil during its oxidation by atmospheric oxygen.

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Note: Figure translations are in progress. See original paper for figures.