INHIBITION OF THE OXIDATION OF SYNTHETIC OILS AT HIGH TEMPERATURES

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This work represents an attempt to study the action of certain compounds of the phenol and amine type as inhibitors of the oxidation process at high temperatures. According to data reported in [1, 2], the presence of several benzene rings with aliphatic side chains in the inhibitor molecule will decrease its volatility and increase its oil solubility.

On this premise, we have carried out the directed synthesis of the following compounds: N,N'-bis-(methoxyphenyl)-p-phenylenediamine (I); 2,4-dimethoxybenzylidene-bis-alkylphenol (II); p-hydroxybenzylidene-bis-alkylphenol (III); dicyclohexyl N-p-methoxyphenylaminosuccinate (IV); dioctyl N-p-hydroxylphenylaminosuccinate (V); dibenzyl N-piperidinosuccinate (VI); and dibenzyl N,N'-bis(piperazino)succinate (VII).

These compounds were prepared by methods described previously [3-6]. A brief characterization of these compounds is given in Table 1.

The oxidation of the synthetic oil was carried out in a manometric unit [7]. The oil sample was 1 g, oxidation temperature 230°C. A pentaerythritol ester was used as the synthetic oil.

A comparison of the kinetic curves for the oxidation revealed a certain correlation between the structure of the compounds that were synthesized and their antioxidant capabilities.

Kinetic curves for the oxidation of the pentaerythritol ester with optimal concentrations of these compounds are shown in Fig. 1.

As can be seen from these curves, a compound of the aminophenol type with long alkoxycarbonyl groups (V) is very effective in reducing the oxidation rate of the oil (Fig. 1, curve 9). Also manifesting an inhibiting

TABLE 1. Brief Characterization of Compounds Synthesized

No.	Compound	Melting pt. °C	Refractive index, n_D^{20}	Nitrogen content, %	
				calcd.	found
I	N,N'-Bis(methoxyphenyl)-p-phenylenediamine	77	–	8.74	8.70
II	2,4-Dimethoxybenzylidene-bis-alkylphenol	–	1.5580	–	–
III	p-Hydroxybenzylidene-bis-alkylphenol	–	1.5210	–	–
IV	Dicyclohexyl N-p-methoxyphenylaminosuccinate	122	–	3.47	3.41
V	Dioctyl N-p-hydroxyphenylaminosuccinate	168	–	2.80	2.46
VI	Dibenzyl N-piperidinosuccinate	56	–	3.67	3.29
VII	Dibenzyl N,N'-bis(piperazino)succinate	116	–	4.27	4.14

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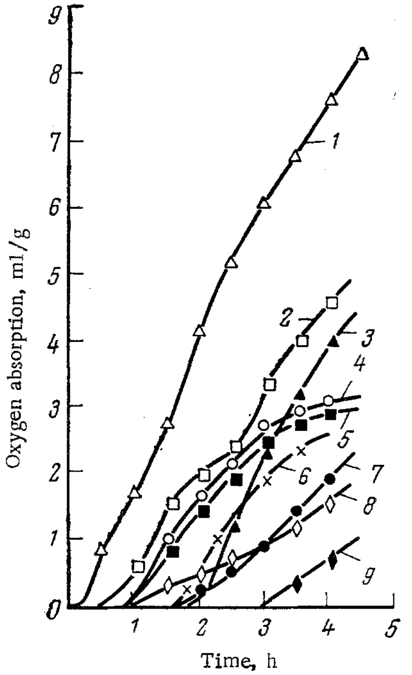

Fig. 1. Kinetic curves for absorption of oxygen by pentaerythritol ester with added inhibitors (oxidation temperature 230°C): 1) pentaerythritol ester (PE) without antioxidant; 2) PE + 0.1 moles-liter* dibenzyl N-piperidinosuccinate; 3) PE + 0.05 moles/liter dibenzyl N,N'-bis(piperazino)succinate; 4) PE + 0.01 moles/liter N,N'-bis-(methoxyphenyl)-p-phenylenediamine; 5) PE + 0.05 moles/liter 2,4-dimethoxybenzylidene-bis-alkylphenol; 6) PE + 0.05 moles/liter dicyclohexyl N-p-methoxyphenylaminosuccinate; 7) PE + 0.05 moles/liter p-hydroxybenzylidene-bis-alkylphenol; 8) PE + 0.1 moles/liter phenyl-α-naphthylamine; 9) PE + 0.05 moles/liter dioctyl N-p-hydroxyphenylamino succinate.

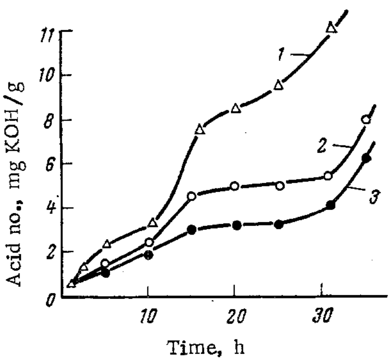

Fig. 2

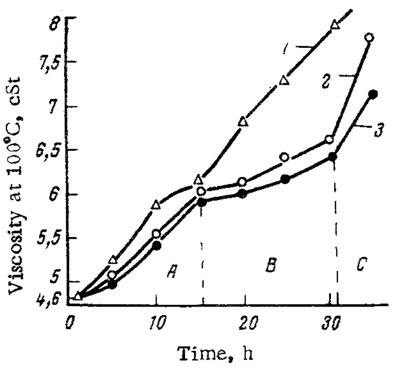

Fig. 3

Fig. 2. Change in acid number during oxidation of pentaerythritol ester with added inhibitors (oxidation temperature 230°C): 1) pentaerythritol ester (PE) without inhibitor; 2) PE + 0.01 moles/liter dibenzyl N, N'-bis(piperazino)succinate; 3) PE + 0.01 moles/liter dioctyl N-p-hydroxyphenylaminosuccinate.

Fig. 3. Change in viscosity during oxidation of pentaerythritol ester with added inhibitors (oxidation temperature 230°C). Curve numbers same as in Fig. 2.

effect under these oxidation conditions are the p-hydroxybenzylidene-bis-alkylphenol, the dibenzyl N,N'-bis-(piperazino)succinate, and the dicyclohexyl N-p-methoxyphenyl aminosuccinate.

These compounds (curves 3, 6, 7, and 9) give greater increases in induction period of the synthetic oil than that given by an antioxidant additive of the phenyl-α-naphthylamine type (curve 8).

Comparing the oxidation curves 5 and 7, we see that, when the methoxy groups in the 2,4-dimethoxybenzylidene-bis-alkylphenol are replaced by a hydroxyl group, the p-hydroxybenzylidene-bis-alkylphenol is considerably better in antioxidant properties. The dibenzyl N,N'-bis(piperazino)succinate is more effective than the dibenzyl N-piperidinosuccinate, apparently because of the presence of the second nitrogen atom and the greater molecular weight.

In Figs. 2 and 3, we show curves for the change in acid number and viscosity of the synthetic oil when oxidized at 230°C with and without inhibitors, in the presence of copper, steel, and aluminum strips. In these test, dry air was bubbled at a rate of 50 ml/min through 50-g oil samples.

All of the kinetic curves proved to be almost identical in character.

The apparent passivity of the inhibitor in section A of the curve (see Fig. 3) can evidently be explained on the basis that, at the start of the oxidation, the viscosity change is caused mainly by evaporation of the readily volatile part of the oil. In section B (Fig. 3), the viscosity changes mainly through processes of oxidation (gum formation). The sharp increase in viscosity in section C of curves 2 and 3 is explained on the basis that the inhibitor no longer has any effect on the oxidation process.

Thus we see that these compounds, which have been proposed as inhibitors, are effective in improving the stability of this synthetic oil at 230°C.

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PROCESS KINETICS OF NEUTRALIZATION OF FATTY ACIDS FROM OXIDIZED PARAFFIN WITH AQUEOUS SODIUM HYDROXIDE SOLUTION

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An account was given in [1] of the overall kinetic relationships for the consumption of sodium hydroxide in the saponification of catalytically oxidized solid and liquid paraffins, on the basis of the saponification number. Here we are reporting on a study of the kinetics of neutralization of the free fatty acids in the oxidized product with sodium hydroxide.

The starting materials were certain individual fatty acids, i.e., acetic (GOST 61-51, "ch.d.a." [analytic] grade), valeric (MRTU 6-09-2525-69), pelargonic (TU 6-09-571-70), lauric (MRTU 6-09-995-64), palmitic (TU MKhP-2936-51), and arachidic (TU NCh-11-64), as well as catalytically oxidized solid paraffins (GOST 16960-71) and liquid paraffins (TU 31-1-01-112-71). The characteristics of these last two products are listed in Table 1.

Since the lauric, palmitic, and arachidic acids and the oxidized product from the solid paraffin are solids at normal temperatures, each of the acids and oxidized products was blended in a C_{12}-C_{14} cut of paraffinic hydrocarbons in amount sufficient to give an acid number of about 20 mg KOH/g; these solutions were all liquids at normal temperatures.

In order to increase the solubility of the palmitic and arachidic acids, pelargonic acid was added to these materials, in respective mole ratios of 1/1 and 2/1.

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