DEGREE OF ESTERIFICATION OF PENTAESRYTHRITOL
ESTERS OF CARBOXYLIC ACIDS IN RELATION
TO THERMAL-OXIDATIVE STABILITY

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One of the primary criteria in selecting base oils and additives is their resistance to oxidation by atmospheric oxygen at elevated temperatures in the lubrication of moving parts.

In the lubrication of modern aviation engines, widespread use is made of oils based on the pentaerythritol esters of monocarboxylic acids (PEE). The relative oxidation stability of PEE at high temperatures (up to 200°C) is governed by molecular structure of these compounds.

The lower reactivity of the PEE molecule toward atmospheric oxygen in comparison with that of hydrocarbon molecules is explained by the deactivating effect of the oxygen in the alkoxy functional group toward the C-H bond of the acyl group. Evidently the strength of the C-H bond of the acyl group that is in the α position relative to the alkoxy group may depend on various changes in the PEE structure. In particular, it is of great theoretical and practical interest to study the influence of unesterified hydroxyl groups in the PEE molecule on its thermal-oxidative stability.

In investigating the influence of the concentration of unesterified hydroxyl groups on the thermal-oxidative stability, we oxidized two samples of pentaerythritol caproates with different degrees of esterification. The degree of esterification of each of these esters was evaluated in terms of the hydroxyl number (calculated for triester*): for the first sample it was 100%, and for the second sample 88% [1, 2].

The thermal-oxidative stability was evaluated by oxidizing the samples in a static manometric unit (Fig. 1), consisting of a set of identical systems, each of which includes a reaction vessel 6 and a differential manometer 5. The reaction vessel is a glass tube with the end expanded to form a flat bottom, so as to form a uniformly thin layer (1.5 mm) of the sample being oxidized [3]. The oxidation was performed at 200°C. The amount of oxygen absorbed was determined from the drop in pressure as measured on the differential manometer 5.

Kinetic curves are presented in Fig. 2 for the oxidation of the PEE samples. It will be seen that the PEE was oxidized without any appreciable induction period. In the initial oxidation period, the oxygen absorption rate was quite high; after 70 minutes of oxidation, it started to drop off considerably, and within 180 min had fallen to very nearly zero. From the nature of these kinetic curves it is evident that the completely esterified PEE sample was oxidized at a higher rate than the incompletely esterified material. From the structure of the molecule, it appears quite improbable that the introduction of oxygen at a C-H bond in the α or β position with respect to the alkoxy group would be any easier in the completely esterified material than in the ester containing one or two unesterified hydroxyl groups. Evidently the oxidation of PEE at 200°C is accompanied by thermal-oxidative breakdown with the formation of low-molecular-weight volatile products that affect the oxygen absorption results.

In order to test this assumption, vibrational spectra were investigated for the PEE samples with different degrees of esterification, before and after oxidation. The PEE samples were oxidized by the method described previously, for a period of 70 min. This made it possible to select the most active section on the kinetic absorption curve and limit the influence of secondary oxidation products.

*As in Russian original — Translator.


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To pump Oxygen

Fig. 1. Static manometric unit: 1, 2, 3) stopcocks; 4) mercury manometer; 5) differential manometer; 6) reaction vessel; 7) bath.

Fig. 2. Kinetic curves for oxidation of pentaerythritol caproates with following degrees of esterification: 1) 100%; 2) 88%.

Fig. 3. Vibrational spectra of pentaerythritol caproates: a) degree of esterification 100%; 1) before oxidation; 2) after oxidation. b) Degree of esterification 88%; 1) before oxidation; 2) after oxidation.

Vibrational spectra are shown in Fig. 3 for the PEE samples before and after oxidation. The spectra were obtained in a UR-20 spectrophotometer in NaCl cuvettes with an absorbing layer 20 mm thick. From an analysis of the spectral data it follows that the oxidation produced in both samples a greater intensity of the bands in the 3540 and 3580 cm⁻¹ region for hydroxyl groups. There were also increases in the intensity of the bands for C = O and C−O bonds in the region at about 1710 and 950 cm⁻¹ [4, 5]. The increases in these band intensities indicate that the decomposition of hydroperoxides is accompanied by the formation of alcohols and acids. The absorption of rocking deformation vibrations of C−H bonds of methylene groups in the region near 740 cm⁻¹ characterizes the presence of C₅ alkyl radicals in the pentaerythritol ester of hexanoic acid. Evidently the appearance of new absorption bands of methylene groups in the spectrum (760 and 780 cm⁻¹ region) after oxidation of the esters may be explained by breakdown of the alkyl radical, and the decrease in intensity of the 740 cm⁻¹ band, by a corresponding decrease in concentration of the C₅ radical.