The formation of the bisphenol through reaction (16) was observed in [7] in the interaction of Ionol in benzene solution with the cyclohexyloxyl radical in the absence of oxygen at 70°C. The bisphenol is a more effective antioxidant than the Ionol. Thus, in contrast to the situation in solutions of Ionol in n-octane, in which destruction of the In- radicals leads to the consumption of antioxidant, the destruction of 2,6-di-tert-butyl-4-methylphenoxyl in aromatic hydrocarbons through reaction (16) leads to regeneration of an antioxidant. It should be kept in view that the destruction of In- radicals in n-octane is directly related to the retardation of oxidation, whereas in toluene it is an intermediate act that is unrelated to breaking the oxidation chains.

The differences that we have established between the conversions of Ionol in n-octane and in toluene have provided an explanation of the reason for the differences in efficiency of Ionol in original and dearomatized fuels and oils. The existence of reactions (11) and (16) provides an explanation, in the theory of inhibited oxidation of hydrocarbons, for the deviations from integral values that are observed in the coefficient accounts for the number of cases of chain breaking by one molecule of antioxidant [1, pp. 110-115]. The difference between the rates of formation and destruction of In- radicals in toluene, and in n-octane at temperatures above 160°C, along with the selective destruction of In- radicals in paraffinic and aromatic hydrocarbons through reaction (12) or reaction (16) with regeneration of antioxidant, explain the reasons for the deviation of the In- concentration from the quasistationary value. In this connection, the method of stationary concentrations (Bodenstein method) can be applied to In- radicals only in those cases in which the In- radicals are formed and destroyed primarily through interaction of InH and In- with the active radicals carrying the oxidation chain.

LITERATURE CITED


MECHANISM OF FORMATION OF FRICTION POLYMERS IN LUBRICATING OILS


In a lubricating oil medium with added monomers [1-3] that can enter into a polymerization or polycondensation reaction, or in a glycerol medium under certain conditions [4], polymeric films are formed on the rubbing surfaces. The opinion has been expressed that tri polymers give substantial improvements in the antifriction, antiscoring (extreme-pressure), and antiwear properties of lubricating oils [2].

Here we are reporting on an investigation of the conditions and mechanism of formation of a tri polymer film, and a determination of the extent to which it affects the wear resistance of rubbing pairs. The tribometric tests were performed in an end-surface friction tester [5] with moving specimens made of Br. OF 6-0.25 [phosphor bronze] and fixed specimens made of Grade 45 steel [similar to 1045 carbon steel]. During the tests, the specific load at seizure \( P_{\text{max}} \) and the coefficient of friction \( f \) were measured. The wear was determined by weighing the specimens. The test time was 5 h, and the bulk oil temperature under steady-state friction conditions was 50-60°C.

The formation of a polymeric film was observed when the test lubricant was either a water-glycerol mixture, an ester, or a solution of an ester in white mineral oil. The film thickness was measured by means of an ITP-69 instrument. The specimen surfaces, after vacuum-coating with gold, were photographed by means of a JSM-35 scanning electron microscope with an accelerating voltage of 25 kV. In the water-glycol mixtures, the film that was formed by the friction was hydrophilic and would absorb dyes; in monoalkyl or...
dialkyl esters of carboxylic or hydroxycarboxylic acids, or in solutions of these esters in mineral oil, the film was not water-wettable, but it did absorb dyes. In all of the experiments, the thickness of the tribopolymer film was 1-3 μm.

On the surface of the steel specimen after the friction test in dioetyl adipate, a tribopolymer film with a fibrillar structure was formed (Fig. 1, views a-c), which is characteristic for polymers crystallizing in the hedrite type. A number of polymers recrystallized from solution have a similar structure [6]. The character of mechanical failure of the polymer films is cohesive, without any signs of delamination, indicating a high degree of adhesion of the polymer to the metal substrate.

In [1], a radical mechanism was suggested for the formation of a tribopolymer film in vapors of organic compounds, but no experimental evidence was presented. In our opinion, the radical process is also the most probable in the polymerization of esters under conditions of friction. Experimental support for this view can be obtained by adding to a lubricating medium either an initiator or an inhibitor of radical polymerization. If the process of tribopolymer film formation is actually a radical process, the initiator should make it easier to form the polymer and hence improve the lubricity, and the inhibitor should prevent tribopolymerization and hence have a very adverse effect on the antiwear properties of the fluid.

In Table 1 we present data on the lubricating properties of a 30% solution of dinonyl adipate in mineral oil, with various added amounts of a radical polymerization initiator (a stable radical of the carborane series, designated A) or an inhibitor which was either hydroquinone (E) or 2,6-dibutyl-4-(C-carboranyl)-phenol (C). These data show a considerable improvement in lubricity of the ester formulations with increasing concentration of the radical polymerization inhibitor, and a considerable drop in lubricity with increasing concentrations of the inhibitors. No polymeric film was found on the specimens after testing in the media containing inhibitors. These results suggest a radical mechanism for the tribopolymerization of esters.

It is known that in friction, because of local increases in temperature and pressure, suitable conditions are created for various tribochemical processes in a lubricating medium. Since the experiments we have just described were carried out in air, the investigation of the chemical reactions in the friction zone was complicated by the presence of oxygen.

The good lubricity of esters is explained by the formation of a protective polymeric film on the rubbing surfaces. Therefore, the reactions that lead to the formation of a tribopolymer with a characteristic crystal structure (Fig. 1) are of the greatest interest. Only regular polymers are capable of crystallization.

Considering the chemical composition of the lubricating medium, which consists of an ester and the products of its tribochemical conversion, it is highly probable that the ester takes part in the tribopolymerization process. Esters can be polymerized through the carbonyl bond [7]. The tribopolymer thus formed on the rubbing surfaces should have the chemical structure of a polyether. If the tribopolymer composition included significant amounts of products from tribochemical conversions of the original ester, the polymer chains thus formed would not have a regular structure and would not be capable of crystallization.

In investigating the influence of the chemical composition of the tribopolymer films on the lubricating and antiwear properties of fluids, we carried out experiments in which monomers of the methacrylate series...