Reciprocal Influence of Succinimide and Oligodiene- and Oligoolefin-Based Sulfur-Containing Alkylphenols

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ABSTRACT: Reciprocal influence of antioxidizing and detergent-dispersive components of batch additives have been studied. Oligomers of piperylene and isobutylene functionalized by element sulfur and phenols in combination with succinimide have been chosen as the object of research. Constants of inhibition rates have been determined for oligomer antioxidizing agents. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1842–1846, 2007

Key words: oligomer; additives; property; antioxidant

INTRODUCTION

Batch additives to various lubricating agents enjoy a steady increase in demand. The deterging components, succinimide for instance, are used in oils with antioxidizing and antiwear additives.[1] As separate additives possess operational properties to a different extent, the optimal overall quality is obtained at proper combination considering their effect and selection of appropriate compositions.[2] The effect of succinimide as a detergent, phenol-based oxidation inhibitors, and chemical additives of polyfunctional action were studied for their washing and antioxidizing properties.

EXPERIMENTAL

As antioxidizing reagents and additives of multipurpose action phenol- and element sulfur-modified piperylene ($\overline{M}_n = 910$) and isobutylene ($\overline{M}_n = 390$; 880) oligomers : 4-oligopiperyleneylphenol, 4-oligoisobutenylphenol, 2,6–di-*tert*-butyl-4-oligopiperenylphenol, 2,6-di-*tert*-butyl-4-oligoisobutenylphenols; sulfated oligopiperylene (OPP), oligopiperelenylphenols, and oligoisobutylenes (OIB); 2,2′-thio-*bis*-(4-oligoisobutenylphenols) were used.[3] Succinimide was synthesized on oligoisobutylene ($\overline{M}_n = 880$) according to method reported in Ref. 1, and the nitrogen content in it came to 3.98 wt %, that corresponds to bissuccinimide structure. Washing action of imides of amber acid, whose molecule include groups of high polarity and hydrocarbon oleophilic part characterized by great affinity to oil was considered in the aspect of their solubilizing capacity, i.e., transfer by SAS micelle in a solution of products, insoluble in the given environment. Research into solubilizing ability of modified substances in iso-octane environment was done by a technique described in Ref. 4.

Antioxidizing activity of the samples was measured on the rate of oxygen absorption in radical chain process of isopropylbenzene (IPB) oxidation with universal manometer apparatus (the relative error of reading is not more than 10%) at the initiation rate of $V_i = 7.21$ 10^{-8} (mol/L s) and temperature of 333 K in kinetic regime. Azodiisobutyronitrile (AIBN) was used to initiate the oxidation. The kinetic purity of IPB was estimated by comparing specially measured oxidation parameter $k_2/\sqrt{2k_6}$ with data given in literature (k_2 and k_6 are rate constants of oxidation chain growth and breakage considering cumylperoxile radicals of IPB). In practice, this value is $k_2/\sqrt{2k_6} = (3.2 \pm 0.3) \times 10^{-3}$ (L/mol s) (the correlation factor $r = 0.9953$).[5] The effectiveness of antioxidizing action of the samples was determined on the extent of the reduction of oxygen initial absorption rate in oxidizing the model substrate in sample presence.

To estimate reactivity of tested substances as antioxidants (AO), the effective constant rate of oxidation chain breakage fk_{In} was used, where f is the capacity of inhibitor action, k_{In} the constant rate of oxidation chain breakage on AO molecule. As a reference to be compared with a standard inhibitor, ionol, the value of $fk_{In} = (2.0 \pm 0.2) \times 10^4$ (L/mol s), which is in good coordination with the data,[5] was chosen.

RESULTS AND DISCUSSION

According to Ref. 6, the concentration dependences of antiwear efficiency of sulfur-containing compounds have complex extreme character accounted for by micelle formation in oil solution of the additive. From this point of view, it was interesting to investigate the concentration dependences of compositions in antiwear and detergent-dispersive additives.

In relation to the dye, the solubilizing action was to a greater or lesser extent shown by all types of investigated compounds. The curves of the dependence of composition solubilization effect (SE) on additive concentrations are of a complex extreme character; their arrangement is also varied in relation to the axes of coordinates. In experiments with rhodamine C, mainly two types of curves [Fig. 1(a–c)] were constructed: the first is characterized by fast colloid dissolution of dye and the solution stability (curves 2b, 3b); the other by a longer stabilization period of solutions (curves 2a, 3a), but with a sharp growth of solubilization effect for compositions in the area of the higher concentration (curve 9a).

In compositions of these additives, the solubilizing effect rises and critical values of concentrations for micelle formation (CCM) are shifted to the region of their reduction as compared to individual substances in isooctane (Table I).

According to the Traube-Duclo rule, influence on succinimide detergent-dispersive action of size and
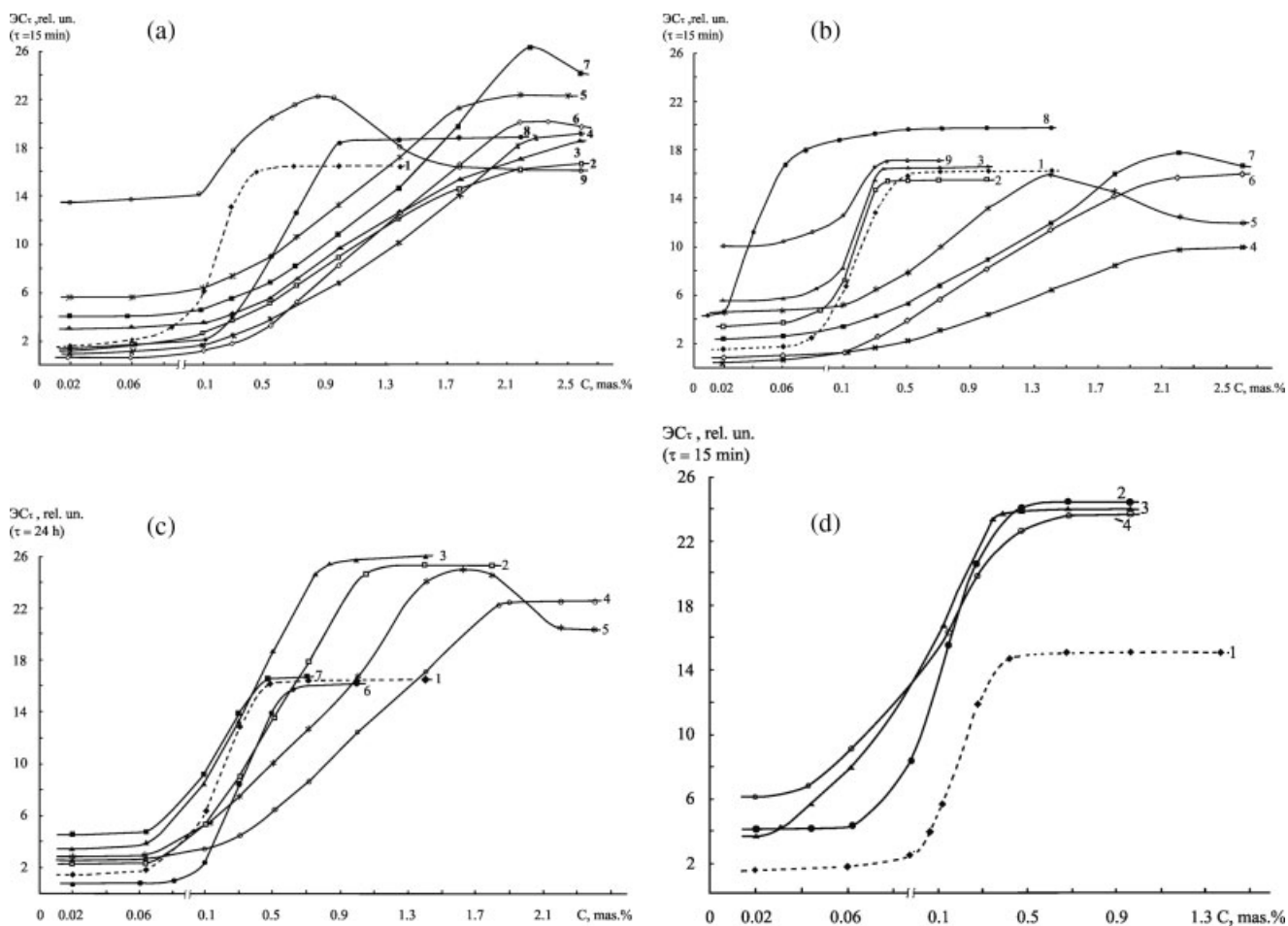
Figure 1 The dependence of solubilizing ability on additive concentration in solution. (a) Modified OIB ($M_n = 880$): 1 – succinimide; 2 – sulfated OIB; 3 – sulfated OIB – succinimide (0.3 wt %); 4 – 2,6-di-*tert*-butyl-4-oligoisobutenylhenol; 5 – 2,6-di-*tert*-butyl-4-oligoisobutenylphenol-succinimide (0.3 wt %); 9 – 2,6-di-*tert*-butyl-4-oligoisobutylenphenol: sulfated oligoisobuty-lene, wt % = 1 : 1; 7 – 2,6-di-*tert*-butyl-4-oligoisobutenylphenol: sulfated oligoisobutylene, wt % = 1 : 1 – succinimide (0.3 wt %); 8 – 2,2′-thio-*bis*-4,4′-oligoisobutenylphenol; 9 –2,2′-thio-*bis*-4,4′-oligoisobutenylphenol – succinimide (0.3 wt %). (b) Modified OIB ($M_n = 390$): 1 – succinimide; 2 – sulfated OIB; 3 – sulfated OIB – succinimide (0.3 wt %); 4 – 2,6-di-*tert*-butyl-4-oligoisobutenyl-phenol; 5 – 2,6-di-*tert*-butyl-4-oligoisobutenylphenol – succinimide (0.3 wt %); 6 – 2,6-di-*tert*-butyl-4-oligoisobutenylphenol: sulfated oligoisobutylene, mass. = 1 : 1; 7 – 2,6-di-*tert*-butyl-4-oligoisobutenylphenol: sulfated oligoisobutylene, wt % = 1 : 1-suc-cinimide; 8 – 2,2′-thio-*bis*-4,4′-oligoisobutenylphenol; 9 – 2,2′-thio-*bis*-4,4′-oligoisobutenylphenol – succinimide (0.3 wt %). (c) Modified OPP: 1 – succinimide; 2 – sulfated OPP; 3 – sulfated OPP– succinimide (0.3 wt %); 4 – 2,6-di-*tert*-butyl-4-oligopiper-ylenylphenol; 5 – 2,6-di-*tert*-butyl-4-oligopiperylenylphenol – succinimide (0.3 wt %); 6 – sulfated 2,2-di-*tert*-butyl-4-oligopipery-lenylphenol; 7 – 2,6-di-*tert*-butyl-4-oligopiperylenylphenol – succinimide (0.3 wt %).

TABLE I
Critical Concentration of Micelle Formation in Functionalized Products (wt %)

Additive	OPP $(\overline{M}_n = 910)$	OIB $(\overline{M}_n = 880)$	OIB $(\overline{M}_n = 390)$
Succinimide	0.08–0.42	0.08–0.42	0.08–0.42
Sulfated oligomer	0.09–1.30	0.10–1.90	0.09–0.30
Sulfated oligomer – succinimide (0.3 wt %)	0.08–0.70	0.08–1.70	0.08–0.20
Alkylated 2,6-di-*tert*-butyl-phenol	0.20–1.80	0.30–3.00	0.20–2.20
Alkylated 2,6-di-*tert*-butyl-phenol – succinimide (0.3 wt %)	0.08–1.60	0.10–2.40	0.10–1.40
Product of successive alkylation and sulfiding in nonpolar solvents	0.09–0.56	0.10–2.40	0.16–2.20
Product of successive alkylation and sulfiding in nonpolar solvents – succinimide (0.3 wt %)	0.09–0.30	0.10–2.20	0.08–2.10
Product of successive alkylation and sulfiding in polar solvents	–	0.15–0.95	0.07–1.00
Product of successive alkylation and sulfiding in polar solvents – succinimide (0.3 wt %)	–	0.03–0.09	0.04–0.09

structure of hydrocarbonic radical of antioxidizing and antiwear additives introduced into oil composition is traced. The maximum solubilization effect takes place for the ramified and smaller radicals in size. Such effect is a property of substances synthesized on the basis of OPP ($\overline{M}_n = 910$) and OIB ($\overline{M}_n = 390$). Experimental data (Table I) testify that introduction of the synthesized substances in an oil composition with succinimide allows to substantially lower their dosage to maintain the operational characteristics at a sufficiently high level.

For further studies of succinimide effect on antioxidizing action of oligomers functionalized by sulfur and phenol, the latter were tested for the specified properties.

As a result of experimental studies, all modified OIB and OPP inhibit the process of initiated oxidation of IPB. The bigger starting concentration of samples entering the substrate under oxidation results in naturally lower oxidation rate. The dependences of starting rates of initiated oxidation of IPB on the concentration of the additives of substances under study are given in Figures 2 and 3. In the radical chain oxidation mode of IPB, the value of fk_{In} is employed in eq. (1)[7]:

$$F = \frac{V_0}{V} - \frac{V}{V_0} = fk_{In}[InH]/\sqrt{2k_6 V_i} \qquad (1)$$

where V_0 and V are the starting rates of oxygen absorption in IPB oxidation in the absence and in the presence of AO, respectively, V_i the rate of oxidation initiation, $[InH]$ the concentration of inhibiting additive, k_{In} and $2k_6$ the rate constants of oxidation chain breakage on the inhibitor and quadratic chain break-
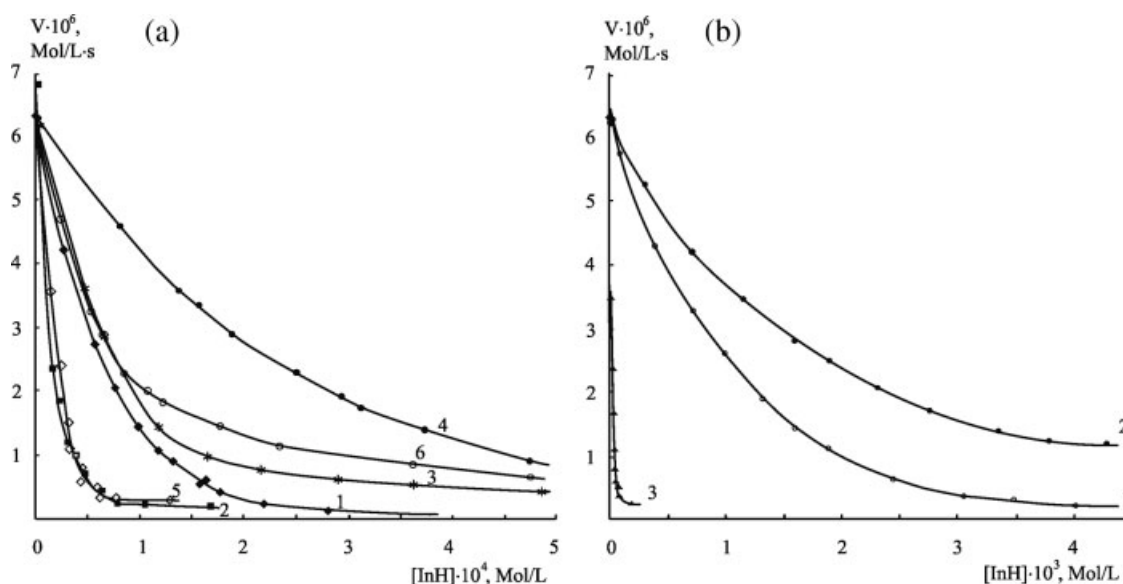
Figure 2 The dependence of cumene oxidation rate on inhibitor concentration: (a) 1. – 4-oligoisobutenylphenol ($\overline{M}_n$ (OIB) = 390); 2. – 2,2'-thio-*bis*-(4-oligoisobutenylphenol), ($\overline{M}_n$ (OIB) = 390); 3. – 4-oligopiperylenylphenol; 4. – sulfated 4-oligopiperylenylphenol; 5. – Ionol. (b) 1. – 4-oligoisobutenylphenol, ($\overline{M}_n$ (OIB) = 880); 2. – 2,2'-thio-*bis*-(4-oligoisobutenylphenol), ($\overline{M}_n$ (OIB) = 880); 3. – ionol.
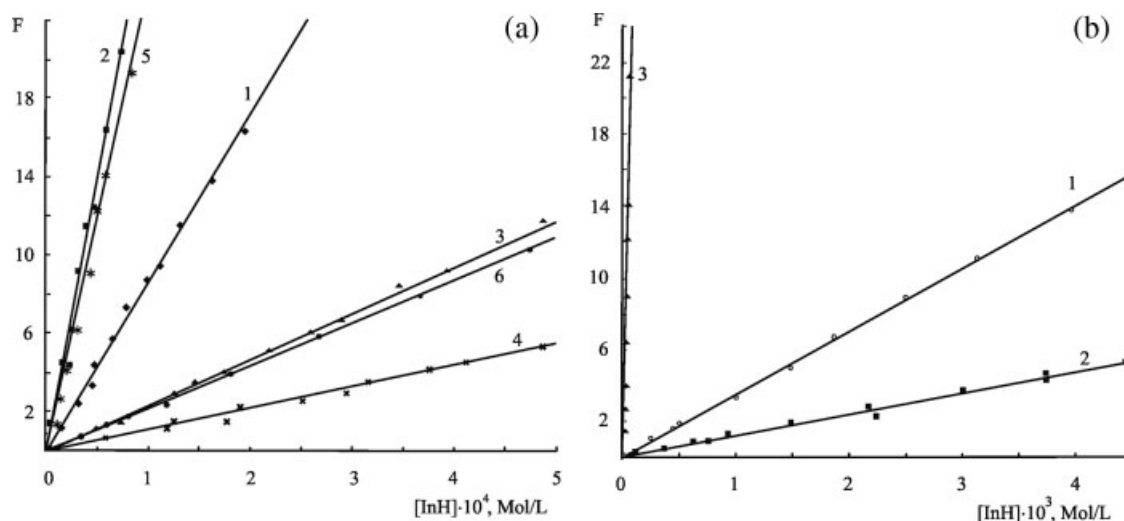
Figure 3 The dependence of inhibitor parameter F on the concentration of inhibitor: (a) 1. – 4-oligoisobutenylphenol, $(\overline{M}_n$ (OIB) = 390); 2. – 2,2′-thio-*bis*-(4-oligoisobutenylphenol), $(\overline{M}_n$ (OIB) = 390); 3. – 4-oligopiperylenylphenol; 4. – sulfated 4-oligopiperylenyphenol; 5. – ionol; 6. – succinimide. (b) 1. – 4-oligoisobutenylphenol, $(\overline{M}_n$ (OIB) = 880); 2. – 2,2′-thio-*bis*-(4-oligoisobutenylphenol), $(\overline{M}_n$ (OIB) = 880); 3. – ionol.

age on cumylperoxile radicals of the substrate respectively.[5] Relationship (1) is established to satisfy all the studied substances (the correlation factor >0.95, Figs. 2 and 3). The linear dependence of inhibition parameter calculated in (1) on the concentration of AO under study testifies that in this interval of concentration quadratic breakage of inhibited IPB chain oxidation prevails.

Having processed the experimental data in the coordinates of eq. (1), effective constants of inhibition rate fk_{In} were established. These values have been compared with the similar constants of chain breakage on the ionol molecule and are given in Table II.

This antioxidizing activity of the tested compounds can be presented as a series: IV < III < VI < V < VII < I < II < VIII.

The experimental data show that succnimide also possesses a property to slow down the oxidation.

Interrelation between structure and antioxidizing activity of sulfur-containing phenol AO is of a complex nature, as inhibiting properties of these compounds are affected by the structure of phenol and sulfur fragments, their number and arrangement against each other. A certain correlation between the degree of intensity of inhibitor effect and the structure of AO molecule is observed: the length of alkyl chain, substitute character of sulfur atom, the number of sulfide and phenol fragments. In a series of oligomer alkylphenols, the value of fk_{In} rises as the length of hydrocarbon radical (OIB, $\overline{M}_n$ = 390) reduces and the number of phenol fragments grows by one macromolecule (OPP). Introduction of sulfur atoms in 4-oligoisobutenylphenol $(\overline{M}_n$(OIB) = 390) positively influence the oxidation parameters, that is being due to heterolytic decomposition of cumylperoxiles. In case of higher-molecular oligomers, sulfur reduces inhibition rate constant, which is probably caused by steric factor and formation of stable radicals.

Combined action of mixtures of succinimide with piperylene and isobutylene oligomers modified by phenol and sulfur has been further investigated. It was shown that mixtures of AO III–VI with succinimide slow down oxidation, somewhat more effectively than individual components in their composi-

TABLE II
Effective Constants of Inhibition Rate, fk_{In}

No.	Inhibitor	[mac]M_n (Orig. oligomer)	$fk_{In} \cdot (10^{-3}$ L/mol s)
I	4-Oligoisobutenyphenol	390	5.30 ± 0.50
II	2,2′-Thio-bis-(4-oligoisobutenyphenol)	390	16.00 ± 1.50
III	4-Oligoisobutenylphenol	880	0.20 ± 0.03
IV	2,2′-Thio-*bis*(4-oligoisobutenyphenol)	880	0.08 ± 0.01
V	4-Oligopiperylenylphenol	910	1.40 ± 0.20
VI	Sulfated 4-oligopiperylenylphenol	910	0.70 ± 0.10
VII	Succinimide	880	2.00 ± 0.20
VIII	Ionol (2,6-di-*tert*-butyl-4-methylphenol)	220	20.0 ± 2.0
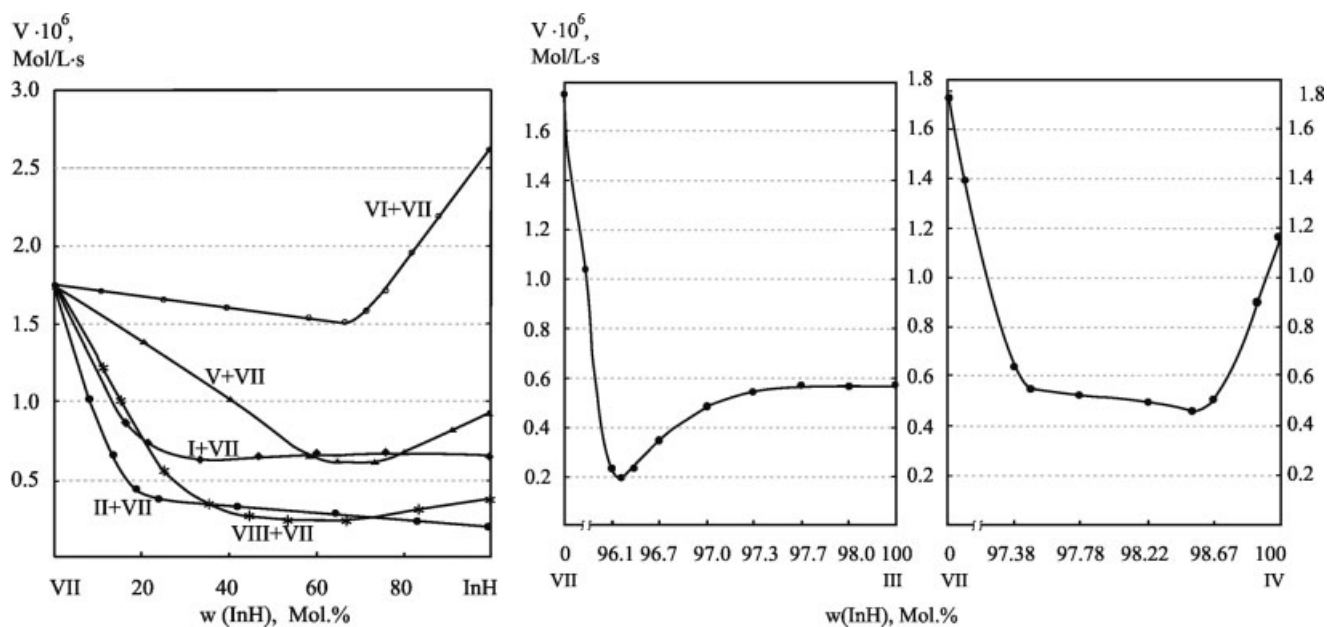
Figure 4 The dependence of cumene oxidation rate on the inhibitor content in the mixture with succinimide: [I + VII] $= 1.5 \times 10^{-4}$ mol/L; [II + VII] $= 1.2 \times 10^{-4}$ mol/L; [III + VII] $= 3.0 \times 10^{-3}$ mol/L; [IV + VII] $= 4.5 \ 10^{-3}$ mol/L; [V + VII] $= 3.0 \times 10^{-4}$ mol/L; [VI + VII] $= 3.5 \times 10^{-4}$ mol/L; [VIII + VII] $= 1.2 \times 10^{-4}$ mol/L.

tion. The dependences of cumene oxidation rate on the inhibitor content in the mixture with succinimide plotted in Figure 4 should be noted as the evidence of lack of any pronounced effect of succinimide on antioxidizing activity of ionol and OIB ($\overline{M}_n = 390$).

Thus, the lack of antagonism in the examined binary mixtures allows to conduct the selection of optimal set of ingredients of batch additives on a smaller number of parameters.

CONCLUSIONS

1. Solubilizing ability of chemical additives on the basis of oligomers of piperylene ($M_n = 910$) and isobutylene ($M_n = 390; 880$), and their effect on detergent-dispersive action of succinimide have been studied; range of critical concentrations of micelle formation have been found. The presence of multifunctional additives allows to considerably decreasing the dosage of washing agent in batch additives.
2. Antioxidizing efficiency of phenol sulfur-containing substances have been studied; fk_{In} for each

one having been computed. Antioxidizing activity of sulfur-containing alkylphenols depends on the structure of sulfur-including fragment, the number and mutual arrangement of S-containing and phenol groups in their molecules.
3. Succinimide in oily composition exerts no marked effect on antioxidizing activity of isobutylene oligomers ($M_n = 390$) modified by element sulfur and phenol.

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