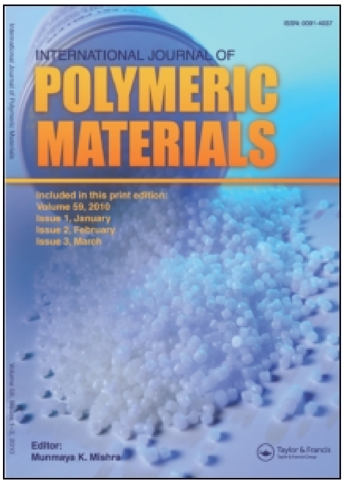

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New Stabilizers for Polymers and Low-Molecular Compounds

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New Stabilizers for Polymers and Low-Molecular Compounds

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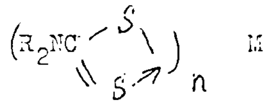
A wide range of compounds whose chelate points contain the S (or Se), N, and O atoms, having different composition and structure of chelate points were investigated with respect to their effectiveness as stabilizers and antioxidants.

KEY WORDS Stabilization, chelates, antioxidants.

In the case of some polymers, stabilizers and antioxidants are found to be an important group of additives capable of preventing the materials from photo- and thermaloxidative degradation in the process of preparation and use of products. For this reason, it is a topical task to search for new classes of effective stabilizers and antioxidants. Inhibition of oxidation processes by metal compounds has received attention of researches, namely, the fact that the metal-containing additives are capable of deactivating the $RO_2^{\cdot}$ radicals (the main chain carriers in the process of self-oxidation of organic compounds in the condensed phase including polymers) as well as, in some cases, these additives catalyze the decomposition of intermediate ROOH hydroperoxides without the resultant free radicals formation. In the literature, much attention was given to the peculiarities and characteristics of the inhibition effect of sulfur-containing chelates of heavy metals, particularly, dithiophosphates and dithiocarbamates of zinc and nickel. One of the aspects of the problem of metal-containing stabilizers concerns the usage of ligands suitable for deactivation of undesirable metal impurities contained by polymers followed by simultaneous formation of the compounds exhibiting the properties of stabilizers (antioxidants).

In the Semyonov Institute of Chemical Physics of the USSR Academy of Sciences, Department of the Kinetics of Chemical and Biological Processes, Laboratory of liquid phase oxidation of organic substrates (head of the Laboratory Dr. I. P. Skibida) for more than 10 years the inhibiting activity of chelate compounds of metals in the oxidation and polymerisation processes, connected with the deactivation of radicals by chelate compounds is being studied by Dr. V. G. Vinogradova and collaborators.[1-3]

A wide range of compounds, whose chelate points contain the S (or Se), N and O atoms, belonging to various classes and having different composition and structure of chelate points as well as different nature of substitutes in ligands has been investigated: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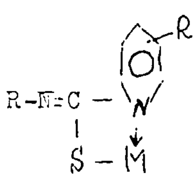
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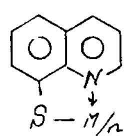
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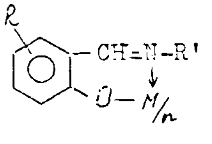
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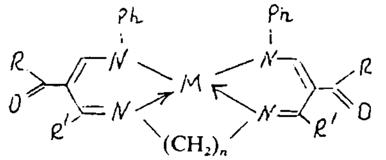
(V)

M-Cu(II), Ni(II), Co(II), Zn(II), Pb(II), Ag(I), Sb(III), Bi(III).

The effect of chelate additives was investigated in self-oxidation of the following model systems: hydrocarbons, polyoxyethylene and its low-molecular analogs in solution at 75–95°C using AIBN as initiator of chain oxidation.

Inhibitory activity of various chelates significantly varies depending on the substrates. Thus in hydrocarbons and ethers only the chelates of types I–III containing the S (Se) atoms in the chelate points exhibit the inhibitory activity. In experimental conditions, inhibition was shown to depend on the deactivation of peroxyradicals $RO_2^{\cdot}$. Some sulfur-containing chelates of Cu(II) and Sb(III) are characterized by very high activity practically independent of the hydrocarbon nature. Relative ligands and their Na salts do not exhibit any inhibitory activity under these conditions. Investigation of kinetic peculiarities of the chelates effect and the composition of their transformation products leads to the assumption that in most cases the inhibition mechanism is determined by the reaction of ligand substitution:

$$ML_n + RO_2^{\cdot} \rightarrow ML_{n-1}(RO_2) + L^{\cdot}$$

$$ML_{n-1} + RO_2^{\cdot} \rightarrow ML_{n-2}(RO_2)_2 + L^{\cdot}, \text{ etc.}$$

$$2L^{\cdot} \rightarrow L_2 \text{ (disulfide)}$$

The oxidation reaction can be realized in the case of Co(II):

$$Co^{II}L_2 + RO_2^{\cdot} \rightarrow Co^{III}L_2(RO_2).$$

The reaction of ligand substitution is assumed to retain the oxidation degree of M in the reaction process. Thus the inhibiting effect of the sulfur-containing chelates of types I–III considerably increases upon introduction of free ligands in the form of LH or NaL due to regeneration of the initial form of the chelate ML_n from its transformation products according to exchange reaction.

When polyoxyethylene (MM 1500–14000) is oxidized in concentrated solutions, the highest inhibitory activity is exhibited by sulfur-containing chelates and the compounds with tetraaza-chelate point (V). Antiradical activity of chelates substantially increases as compared with their effect in the case of hydrocarbons oxidation: the rate constants of interaction with radicals $RO_2^{\cdot}$ increase by more than one order of magnitude for dithiocarbamates of Zn(II) and Bi(III) (complexes of type I). The data obtained indicate that repeated termination of oxidation chains of polyoxyethylene with the participation of Cu(II) and Co(II) chelates and/or their transformation products is possible. Along with the inhibiting function, substituted salicylaldiminates of Cu(II) (IV) exhibit the initiation function which is materialized in catalytic activity of these compounds upon self-oxidation of polyoxyethylene.

The structure of the ligands of the chelates studied does not contain functional groups capable of deactivating the radicals $RO_2^{\cdot}$ due to the classical reaction of the H atom transfer (groups —OH and —NH of the traditional inhibitors belonging to phenols and aromatic amines). According to the authors, the termination of the oxidation chains results from redox-interaction between peroxyradicals and chelate points of complexes. Comparison of the rate constants of chain termination upon interaction of $RO_2^{\cdot}$ with chelates (k_{inh}) and potentials of halfwave of electrochemical oxidation and reduction of chelates ($E_{1/2\ ox}$ and $E_{1/2\ red}$) determined with a voltammeter on the rotating platinum electrode shows that the antiradical activity of chelates and their redox properties are interrelated. Thus, the case of hydrocarbons oxidation shows that absolutely different sets of reactions (in series of sulfur-

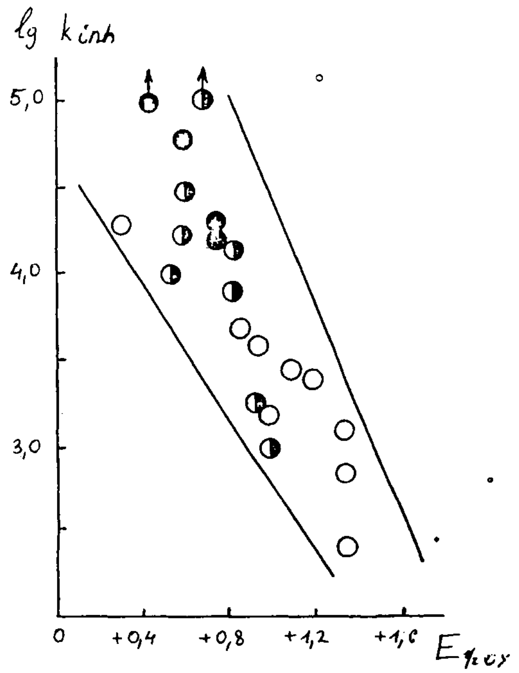

FIGURE 1 Dependence of the inhibition constant k_{inh}(l/mole·s) on the potential of halfwave of electrochemical oxidation $E_{1/2\ ox}$ for sulfur-containing chelates of heavy metals of types I–III (Oxidation of ethylbenzene, 75°C, pressure of O_2 is 1 atm.). ○—I, ◑—II, ●—III.

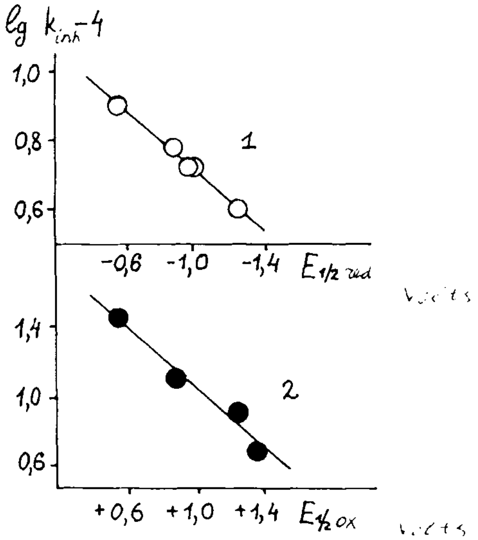

FIGURE 2 Dependence of inhibition constant k_{inh}(l/mole·s) on the potential of halfwave of electrochemical reduction of Cu chelates (type IV) ("I") and the potential of halfwave of electrochemical oxidation of Co chelates (type V) ("2") (oxidation of PE, 75°C, [RH] – 10 M, solvent is chlorobenzene).

containing complexes of one class or formed by one metal) display a common regularity, namely, increasing of chain termination rate constants k_{inh} with a decrease of the potential of halfwave of oxidation E_{ox}, that is, with increasing electron-donor properties of the chelate point (Fig. 1). This correlation has a number of limitations. First, the value $E_{1/2\ ox}$ should have the optimal, though not very low magnitude (complexes with low magnitude of $E_{1/2\ ox}$, as a rule, readily degradate due to the effect of O_2 and do not appear to be effective inhibitors). Second, in some cases the structure of the chelate point and that of the ligands as a whole strongly affect the value k_{inh}. In oxidation of polyoxyethylene (MM 1500) inhibited by chelates of Cu(II), type IV, and Co(II), type V, the magnitudes of k_{inh} increasingly grow depending on the readiness of the oxidation process of tetaaza-chelates of Co and the reduction process of bis(oxa,aza)-chelates of Cu (Fig. 2). In other words, peroxyradicals involved in oxidation of the given polyoxyethylene appear to exhibit dual oxidation-reduction properties.[4,5]

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