On the Mechanism of Interaction of Polymers with Colloidal Metal Particles at the Moment of Their Formation on the Cathode

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On the Mechanism of Interaction of Polymers with Colloidal Metal Particles at the Moment of Their Formation on the Cathode

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When colloidal metal particles are formed on the cathode by the electrolytic method ([1]), and when a solution of a polymer in a hydrocarbon (toluene) is present in the upper layer of the bath, favorable conditions are created for interaction of the polymer with the active centers arising on the fresh surface of such colloidal particles. In this case, the nature of the polymer macromolecules has a substantial influence on the transfer of colloidal metal particles into the upper organic layer of the bath. Thus, in the case of natural rubber or polyisobutylene, the colloidal metal particles do not pass into the organic layer, but are concentrated at the interface between the upper and lower layers of the bath; their transfer into the organic layer becomes possible, as a result of inversion of selective wetting, only upon addition of small amounts of surface-active substances —for example, oleic acid.

If, however, during electrolysis there are polymers with polar functional groups in the organic layer (carboxylated rubber or epoxy resins), the colloidal particles that arise pass into the organic layer in the absence of surface-active substances, thereby forming stable and concentrated metal organosols.

To elucidate the mechanism of interaction of the polymer with the active surface of metal particles, we used the method of infrared spectroscopy.

The objects of study were films of the products of interaction of polyisobutylene, natural rubber, carboxylated rubber, and epoxy resin with colloidal iron particles at the moment of their formation on the cathode by the electrolytic method, as well as films of the indicated polymers obtained by evaporating the upper organic layer after electrolysis carried out in the absence of ferric chloride in the lower layer of the bath.

In addition, infrared spectra were recorded for pure solutions that served as the dispersion medium in obtaining iron organosols with different concentrations of the dispersed phase.

The investigations were carried out on a two-beam infrared spectrophotometer IKS-14 in the region 600–5000 cm^{-1} (NaCl and LiF prisms). The spectrophotometer slit was varied automatically within the range from 66 (4000 cm^{-1}) to

Fig. 1. IR spectra of a 0.5% solution of oleic acid in toluene: (1) the same after 5 min of colloidal iron evolution; (2) the same after 10 min of colloidal iron evolution; (3) the same after 15 min of colloidal iron evolution (4)

Figure 1: Fig. 1. IR spectra of a 0.5% solution of oleic acid in toluene: (1) the same after 5 min of colloidal iron evolution; (2) the same after 10 min of colloidal iron evolution; (3) the same after 15 min of colloidal iron evolution (4)

Fig. 2. IR spectra: a –pure polyisobutylene; b –polyisobutylene + 75% Fe

Figure 2: Fig. 2. IR spectra: a –pure polyisobutylene; b –polyisobutylene + 75% Fe

312 (800 cm^{-1}).

In preparing a film, an equal amount of the colloidal solution of the metal-polymer in toluene was applied to the polished surface of NaCl plates (measuring 34×58 mm), and after complete removal of the solvent the spectra of such films were recorded.

In the case of iron organosols in a 0.5% toluene solution of oleic acid and of the pure dispersion medium of such organosols, the samples studied were placed in standard cuvettes of equal thickness with potassium bromide windows. The results obtained are presented in Figs. 1, 2, 3, and 4.

The presence of even a small amount of colloidal iron in a 0.5% toluene solution of oleic acid causes a substantial decrease in the integral intensity of the band at 1720 cm^{-1}.

An analogous picture was observed by us in studying the IR spectra of organosols of other metals in the same media. Thus, iron, lead, and nickel affect the decrease in the intensity of the band approximately equally.

Fig. 1. IR spectra of a 0.5% solution of oleic acid in toluene (1), the same after 5 min of colloidal iron evolution (2), the same after 10 min of colloidal iron evolution (3), the same after 15 min of colloidal iron evolution (4)

Fig. 2. IR spectra: *a* –pure polyisobutylene, *b* –polyisobutylene + 75% Fe

of the stretching vibrations of $C = O$ groups. The IR spectra obtained provide a certain experimental basis for the following ideas about the mechanism of the processes occurring in the systems studied during electrolysis.

The integral intensity of the band at 1720 cm^{-1}, characterizing the stretching vibrations of the $C = O$ groups, decreases sharply as the concentration of the dispersed phase of iron organosols in a 0.5% toluene solution of oleic acid increases (Fig. 1). This indicates a decrease in the number of free $C = O$ groups in the solution, caused by chemisorption of oleic acid molecules and their orientation on the surface of colloidal metal particles. Owing to this, a sharply pronounced lyophilization of these particles with respect to toluene occurs, which promotes

Fig. 3. IR spectra of carboxylated rubber (1). 2—the same + 16% Fe, 3—the same + 40% Fe, 4—the same + 46% Fe

Figure 3: Fig. 3. IR spectra of carboxylated rubber (1). 2—the same + 16% Fe, 3—the same + 40% Fe, 4—the same + 46% Fe

Fig. 4. IR spectra of epoxy resin (1). 2—the same + 10% Fe, 3—the same + 20% Fe

Figure 4: Fig. 4. IR spectra of epoxy resin (1). 2—the same + 10% Fe, 3—the same + 20% Fe

their rapid transfer into the upper organic layer of the bath and the formation of an organosol.

The IR spectra of the products of interaction of polyisobutylene and natural rubber with colloidal iron particles, obtained under the conditions of a two-layer electrolytic bath in the presence of oleic acid, do not show any substantial changes in comparison with the IR spectra of films of pure polyisobutylene and natural rubber.

The latter were obtained under the same electrolysis conditions, but in the absence of $FeCl_2$ in the lower layer (Fig. 2, *a*, *b*).

A certain difference in the intensity of the bands at frequencies of 1000-1100 cm^{-1} is explained by different degrees of oxidation.

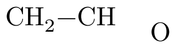
This indicates that macromolecules of polyisobutylene and natural rubber for the most part do not come into direct contact with the surface of the colloidal metal particles, but interact only with the chemically fixed adsorption layers of oleic acid on this surface.

Fig. 3. IR spectra of carboxylated rubber (*1*). *2*—the same + 16% Fe, *3*—the same + 40% Fe, *4*—the same + 46% Fe.

Fig. 4. IR spectra of epoxy resin (*1*). *2*—the same + 10% Fe, *3*—the same + 20% Fe.

These layers are oriented with their hydrocarbon radicals toward the toluene solutions of polyisobutylene and natural rubber, which favors solvation of the surface of the colloidal metal particles by macromolecules of the indicated polymers and the emergence of a structural-mechanical stability factor ([2]-[4]).

Comparison of the IR spectra of films obtained from toluene solutions of carboxylated rubber and epoxy resin with the IR spectra of films of the same polymers filled with colloidal iron obtained by the electrolytic method in the absence of oleic acid shows that the integral intensity of the bands at 1720 cm^{-1} and 915 cm^{-1}, corresponding to the groups C=O and



$$\mathrm{CH_2{-}CH}\quad \mathrm{O}$$

decreases significantly as the concentration of colloidal iron increases (Figs. 3, 4).

This gives grounds to suppose that the functional groups present in the macromolecules of carboxylated rubber and epoxy resin, directly

interact with the surface of colloidal particles at the moment of their formation on the cathode. Such interaction has a sharply pronounced character of chemisorption. The interaction products thereby formed are two-phase, but highly homogenized and stabilized (aggregatively stable) systems. Such systems may appropriately be called metallopolymers, in contrast to two-phase systems in which there is no chemical interaction between polymer macromolecules and the surface of particles of the dispersed metal.

As a result of the experiments carried out, it may be assumed that the type of bond arising upon the interaction of polymer macromolecules with colloidal metal particles at the moment of their formation by the electrolytic method depends mainly on the chemical nature of these polymers.

When polar groups are present in the macromolecules of such polymers, they can interact directly with colloidal metal particles, forming the corresponding surface chemical compounds.

The considerations set forth are also confirmed by studies of the desorption of polymers from the interaction products of natural rubber, polyisobutylene, carboxylate rubber, and epoxy resin with colloidal iron.

As a result of these studies it was established that polyisobutylene is reversibly adsorbed on the surface of colloidal iron particles, whereas carboxylate rubber and epoxy resin are adsorbed on the surface of such particles irreversibly.

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