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Abstract

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ON SOME ELECTROPHYSICAL PROPERTIES OF POLYMERIC COMPLEXES OF TETRACYANOETHYLENE WITH METALS

(Presented by Academician A. N. Frumkin, 13.VIII.1960)

It was shown earlier that, upon the interaction of tetracyanoethylene with metallic powders and metal salts, polymeric chelate compounds are formed, apparently of an azoporphyrin structure (^{1}). Polymeric chelate compounds of tetracyanoethylene with metals are insoluble in ordinary organic solvents, alkalis, and dilute acids. These substances do not melt, withstand many hours of heating at $t = 500°$, possess interesting magnetic properties, and show broad (600-800 oersted) and narrow signals in e.p.r. spectra. The infusibility and insolubility of the polymeric chelates of tetracyanoethylene, as also, indeed, of other polychelate compounds (^{2}), complicate their study and processing. In this connection, the recently proposed method for obtaining coatings and plastics based on polymeric chelates of tetracyanoethylene and its mixtures with di- and tetranitriles (^{3}) is of theoretical and practical interest.

Fig. 1. Infrared spectrum of the polychelate copper complex

In the present work, data are presented from a study of the electrophysical properties of films of polymeric chelate compounds of tetracyanoethylene with metals, chemically bound to the metal, obtained by treating the surface of plates of copper, iron, nickel, and a number of other metals with tetracyanoethylene vapors.

Degreased metal plates, and in some cases additionally subjected to electropolishing and etching, were placed in a vessel with tetracyanoethylene, after which the air was pumped out of the vessel to 10^{-5} mm Hg. The reaction was carried out at temperatures from 150 to 400° for 5-20 hours, as a result of which a film of polymeric complex firmly bound to the metal was formed on the surface.

Structural scheme of the polymer complex

Figure 2: Structural scheme of the polymer complex

Fig. 2. Dependence of the specific conductivity on reciprocal temperature for a film of the polymer complex on etched iron at 300°, 10 h.

Figure 3: Fig. 2. Dependence of the specific conductivity on reciprocal temperature for a film of the polymer complex on etched iron at 300°, 10 h.

The samples obtained in this way were subjected to further investigations without additional treatment. The thickness of the films was determined on the basis of the value of the specific weight of the polymer and the weight of the film. In experiments carried out with iron, the thickness of the film of the polymeric complex, depending on the surface-treatment conditions, was from $5 \cdot 10^{-6}$ to $3 \cdot 10^{-5}$ cm. The films obtained are very difficult to burn, as a consequence of which, according to microanalysis data, the carbon content is somewhat underestimated. Thus, for the polychelate copper complex:

Found, %: C 43.66; Cu 20.62
Calculated, %: C 45.66; Cu 19.88

Investigation of the IR spectrum of the film*, obtained on copper (Fig. 1), showed the complete absence of absorption maxima in the region 800–2300 cm^{-1}, which apparently indicates a paraketone-type structure of the polymer obtained, which can probably be represented by the following scheme:

The electrophysical properties of the films were studied by means of an alternating-current bridge with a capacitance and a resistance connected in parallel, in the range from 200 Hz to 0.2 MHz.

Mercury was poured into a test tube ending in a ground joint into which two wires had been sealed. To one wire was attached a plate immersed in the mercury and coated with the polymer complex, while the other wire served to make contact between the mercury and the measuring circuit. Thus, the film of the polymer complex played the role of the dielectric in a capacitor whose plates were the metal plate and the mercury.

Fig. 2. Dependence of the specific conductivity on reciprocal temperature for a film of the polymer complex on etched iron at 300°, 10 h.

The measurements were carried out at a pressure of 10^{-5} mm Hg. The presence of air, as a rule, substantially changes the results of the measurements and will be investigated further.

The specific conductivity and capacitance of films of the polymer complex were measured as functions of temperature, heating time, and the method of treatment of the metal surface. When iron plates were heated in tetracyanoethylene vapors at 250° for 3 h, comparatively thin ($3 \cdot 10^{-6}$ cm) films of the polymer com-

Fig. 3

Figure 4: Fig. 3

Fig. 4

Figure 5: Fig. 4

plex were obtained, with a specific conductivity of the order of $3 \cdot 10^{-9}\ \Omega^{-1} \cdot \text{cm}^{-1}$ and an effective dielectric constant at a frequency of 3000 Hz, calculated from the formula for a parallel-plate capacitor, equal to 7. When these plates, coated with the polymer film, were heated under the same conditions for another 3 h, their specific conductivity increased to $3 \cdot 10^{-8}\ \Omega^{-1} \cdot \text{cm}^{-1}$, and the value of the effective dielectric constant increased to 36. Changing the temperature of treatment of the pla-

* The authors express their sincere gratitude to Yu. Sh. Moshkovskii and N. D. Kostrova for recording and studying the IR spectrum.

increase from 250 to 450° at the same duration, equal to 10 h, leads to an increase in the specific conductivity, which ranges from $5 \cdot 10^{-8}\ \Omega^{-1} \cdot \text{cm}^{-1}$ to $5 \cdot 10^{-6}\ \Omega^{-1} \cdot \text{cm}^{-1}$, while the value of the effective dielectric constant reaches 70. From the sign of the thermo-e.m.f. it follows that the films have *p*-type conductivity.

Figure 2 presents the dependence of the specific conductivity on reciprocal temperature for films of the polymer complex on iron. The measurements were carried out in the temperature interval from −40 to +220°. Two rectilinear sections are clearly visible on the curve. The first section, corresponding to temperatures from −40 to +30°, corresponds to an activation energy of 0.07-0.12 eV. The second section corresponds to the temperature from 30 to 250° and corresponds to an activation energy of 0.21-0.28 eV. The observed dependence of the logarithm of the specific conductivity on reciprocal temperature is analogous to the dependence on $1/T$ for semiconductors possessing impurity conductivity.

Fig. 3. Dependence of the effective dielectric constant (1) and resistance (2) on the logarithm of frequency for a film of the polymer complex on etched iron, 250°, 10 h.

We also measured the dependence of the effective dielectric constant and resistance of the samples on the logarithm of the alternating-current frequency in the range 400 Hz-0.2 MHz. The corresponding curves are presented in Fig. 3. It should be noted that the capacitance and resistance of the samples fall upon application of a constant voltage, as is seen from Fig. 4.

Fig. 4. Dependence of the capacitance (2) and resistance of a film (1) of the polymer complex on the application of a constant voltage (on air-oxidized iron), 250°, 20 h.

It is also necessary to point out an interesting result obtained with plates coated with a film of the polymer complex. When a direct current is passed through an alcoholic solution of copper sulfate on the polymer film obtained on an iron plate, copper is deposited and adheres firmly to the surface of the polymer complex. The comparatively high values of the effective dielectric constant indicate that we may possibly be dealing with polarization of "conducting" macromolecules.

For the final clarification of the question of the nature of the electrophysical properties of these films, in particular for determining the possible role of structural inhomogeneity, it is necessary to carry out measurements of the effective complex dielectric constant at higher frequencies, which is currently being prepared.

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