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Abstract

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ELECTRICAL PROPERTIES OF SYSTEMS CONSISTING OF POLYMERS AND METALS

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Recently a number of papers and monographs have appeared devoted to the semiconducting properties of organic compounds. In some of these works it has been shown that the introduction of metal atoms into the molecules of complex aromatic compounds affects the physical properties of the latter. Thus Vartanyan ([1,2]) and Ilay ([3,4]) found that atoms of copper and magnesium introduced into phthalocyanine molecules affect the electrical conductivity of these compounds. Topchiev, Geiderikh, Davydov, Kargin, and others ([5]) showed that polyacrylonitrile after heat treatment acquires semiconducting properties in the range from 300 to 900°. At 200° the resistance of polyacrylonitrile is $\sim 10^{12}$ ohm · cm. The introduction of copper salts lowers the resistance to 10^2 ohm · cm (300°).

The purpose of the present investigation was to study the electrical properties of compositions in which metal particles alternate with very thin interlayers of polymers that practically do not conduct current. It was of interest to determine whether, under these conditions, electronic transition is possible, and how the structure of the organic interlayers affects this process.

In connection with the task posed, highly dispersed powdery metals were used. First of all, "semipassive" benzolated iron was employed, obtained by reduction of the oxide in hydrogen at 450–500°. Usually, under such reduction conditions, pyrophoric iron is formed. However, as Burshtein, Pavlova, and Kiperman ([6,7]), as well as Shurmovskaya and Burshtein ([8]), showed, if such iron, after reduction in hydrogen and before contact with air, is immersed in benzene and dried, it loses its pyrophoricity. Benzene adsorbed on the iron prevents the formation of thick oxide films. On the surface of the iron a film is obtained corresponding to one elementary cell of Fe_3O_4. The diameter of the particles of this iron is of the order of tenths of a micron.

The first object of investigation was a composition of the iron described above and polyisoprene (natural rubber), which was introduced from a 2% solution in benzene. Samples in the form of plates were pressed under a pressure of 500–1000 atm. Preliminary experiments on measuring the electrical resistance of these samples showed that even the introduction of 1% polyisoprene into the composition sharply lowers the electrical conductivity of the iron. With a higher rubber content this effect is still stronger.*

The dependence of the logarithm of the electrical conductivity ($\lg \sigma$) on the temperature $\left(\frac{1}{T}\right)$ of a sample containing 20% rubber, in the interval from 50 to $-40°$, proved to be linear; moreover, as the temperature rose the electrical conductivity increased. In the indicated temperature interval the resistance of the sample changed from 11.2 $\Omega \cdot$ cm to 50 $\Omega \cdot$ cm. Such a course of the temperature dependence of electrical conductivity is typical of semiconductors. The thermoe.m.f. and Hall constant of this sample had the same sign as those of p-type semiconductors. The value of the thermoe.m.f. was about 5 μV/deg. The magnitude of the activation energy ΔE, calculated from the equation $\rho = \rho_0 e^{\frac{\Delta E}{kT}}$, was about 0.1 eV. Similar values of the thermoe.m.f. and conductivity were also found for compositions of iron and polystyrene.

From the foregoing it is evident that the composition obtained acquires a number of new properties different from the properties of the components entering into this system. It must also be emphasized that it cannot be assumed that in these systems the electrical conductivity is explained by direct contact of individual metallic particles with one another. In such a case one would observe a temperature dependence of the electrical conductivity characteristic of metals, which is indeed the case for samples pressed from pure powdered iron.

In order to obtain a more uniform distribution of the polymer and a stronger bonding of it with the iron, the work was carried out by the method, developed by V. A. Kargin and N. A. Plate (9), of vibratory grinding of metallic powders in a monomer medium. The essence of this method is that, in the course of comminution, the metal particles, owing to the exposure of fresh energetically active faces, initiate the polymerization of the monomer in the medium in which they are located. At the end of the experiment the polymers formed in the bulk phase are washed away with the appropriate solvents, after which the metallic powder is dried and pressed in the form of plates.

In view of the high dispersity of the iron used by us, it was not possible to expect its further comminution during vibratory grinding. However, under these conditions the exposure of fresh faces should proceed at the expense of damage to, or removal of, the very thin oxide film on the surface of the iron particles.

Table 1

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* The resistance of samples pressed from pure powdery iron is about $1 \cdot 10^{-3}$ ohm • cm; with a rubber content of about 1%, 0.125 ohm • cm; with 5%, 0.127 ohm • cm; 10%, 3.73 ohm • cm; with 20%, 16.18 ohm • cm.

No.	Composition	Temperature interval, °C —from	Temperature interval, °C —to	Change in resistance, $\Omega \cdot$ cm — from	Change in resistance, $\Omega \cdot$ cm —to
1	Iron + polystyrene	150	−63	0.5	21.8
2	Same + polyisoprene	150	−52	0.23	1.77
3	Same + polymethyl methacrylate	150	−45	3.15	87.5
4	Same + polyacrylonitrile	50	−65	0.38	3.88

In these experiments the following monomers were used: isoprene, styrene, methyl methacrylate, as compounds having double bonds, and also acrylonitrile.

For this type of composition, as is seen from Fig. 1, a linear dependence of $\lg \sigma - \frac{1}{T}$ was also observed in the temperature interval from +150 to −55°, with the resistance of the samples in this region changing on average by a factor of 20 (see Table 1). In the region of low temperatures, from −55 to −120°, the curves have a steeper course. The activation energy, expressed in electron-volts, for the various compositions ranged from 0.08 to 0.12. It must be emphasized that, for all compositions obtained by vibratory grinding, the thermoe.m.f. and Hall effect had the same sign as for n-type semiconductors.

type. The magnitude of the thermoe.m.f. is 12–14 μV/deg. As for the Hall effect, it could not be measured in all cases. The Hall constant of the iron–polystyrene composition at room temperature is equal to $2.9 \cdot 10^2$ cm^3/C. In the sample made of iron and acrylonitrile the Hall constant is equal to $4.1 \cdot 10^2$ cm^3/C.

From a comparison of the properties of the compositions obtained by introducing ready-made polyisoprene with those obtained by the method of polymerizing isoprene in a vibratory mill, it is evident that they differ in a number of properties. Thus, in the first case the sign of the conductivity is the same as in p-semiconductors, while in the second case it is the same as in n-semiconductors. The value of the thermoe.m.f. increased from 5 μV/deg to 12–14 μV/deg. The specific resistance in the second case is also greater than in the first. These differences indicate that, apparently, when the compositions are obtained by

Fig. 1. Dependence of the logarithm of electrical conductivity ($\lg \sigma$) on temperature $\left(\frac{1}{T}\right)$. Iron compositions with different polymers: 1 —polymethyl methacrylate; 2 —polystyrene; 3 —polyacrylonitrile; 4 —polyisoprene

Figure 1: Fig. 1. Dependence of the logarithm of electrical conductivity ($\lg \sigma$) on temperature $\left(\frac{1}{T}\right)$. Iron compositions with different polymers: 1 —polymethyl methacrylate; 2 —polystyrene; 3 —polyacrylonitrile; 4 —polyisoprene

the second method the distribution of the polymer is more uniform, and also, possibly, another type of bond is formed between the surface of the metal particles and the organic substance. Elemental analysis showed that the content of total organic substance in the iron-polyisoprene composition (obtained by vibratory milling) is 5.1%, with carbon accounting for 4.53% and hydrogen for 0.56%. In isoprene (C_5H_8) the weight of carbon exceeds the weight of hydrogen by 7.5 times, and in the sample described this ratio is

$$\frac{4.55}{0.56} = 8.$$

Since the ratio of the amounts of carbon and hydrogen is approximately the same as in the monomer, this argues in favor of the fact that the principal reaction in vibratory milling was the polymerization reaction.

Fig. 1. Dependence of the logarithm of electrical conductivity ($\lg \sigma$) on temperature $\left(\frac{1}{T}\right)$. Iron compositions with different polymers: 1 —polymethyl methacrylate; 2 —polystyrene; 3 —polyacrylonitrile; 4 —polyisoprene.

Since the surface of 1 g of iron in our samples was about 1.5 m^2, and the content of organic substance, according to the analysis, was 51 mg, it follows from this (if it is assumed that an adsorbed molecule occupies 25 Å^2 on the surface) that 51 mg is approximately 75 times greater than the amount required to cover the entire surface with a monolayer. This fact also confirms our assumption that during the vibratory milling of iron polymerization of isoprene took place. However, polymerization probably does not proceed over the entire surface of the iron, but only near or on those sites at which, during vibratory milling, the thin oxide film is damaged. Apparently, at these sites the formation of a graft polymer takes place and, judging from the fact that the electrical resistance of the sample (as indicated above) increases*, this polymer covers the iron more or less uniformly; the structure of these interlayers is being clarified. Elemental analysis for the case of compositions with polymethyl methacrylate and polyacrylonitrile gave more complex ratios between the elements. It is possible that, along with polymerization, other reactions also occurred. These phenomena will be investigated in greater detail in the future. At present one may confine oneself to pointing out that the amount of substance bound to the metal exceeds a monolayer by 45 times in the case of methyl methacrylate and by 40 times in the case of acrylonitrile.

At present investigations of the described systems are continuing. Work is also being carried out with systems that include other metals and other polymers, in which electron transfer may occur more readily.

* In comparison with compositions into which polyisoprene was introduced in ready-made form.

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