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THE INFLUENCE OF THE FORM OF AGGREGATION OF DYES ON THE SIGN OF PHOTOCURRENT CARRIERS

In our laboratory, since 1948, the methods of the static capacitor ([1]-[5]) and the vibrating capacitor ([5], [6]) have been used to determine the sign of photocurrent carriers in various semiconductors and dyes. In most cases the results obtained by these methods coincided with the signs of the photocurrent carriers obtained by other investigators using different methods ([7]-[10]). Thus, Vartanyan ([7]) showed that the admission of oxygen characteristically lowers the dark and light conductivity of layers of some dyes and, conversely, raises it for others, which is consistent with the fact that the former are electron semiconductors and the latter hole semiconductors. Meyer ([8]) used this effect of oxygen on the photoconductivity of a large number of dyes to divide them into electron and hole semiconductors. The sign of the dark current carriers for certain dyes was determined from the thermoe.m.f. by Vartanyan and Rozenshtein ([10]) and coincided with the sign of the light current carriers.

By our methods it was also established that a change in the state of aggregation in some dyes not only alters the absorption spectrum and the spectral distribution of the capacitor photo-e.m.f., but also has an effect on the sign of the photocurrent carriers. It turned out that, when amorphous layers of metal-free phthalocyanine with hole conductivity are transformed by thermal activation into the crystalline β-form, the sign of the charge carrier changes from positive to negative ([11]). The negative sign of the photocurrent carrier in a single crystal of the β-form of this pigment was subsequently confirmed by Hall-effect measurements ([12]).

In determining the sign of photocurrent carriers in dyes of the triphenylmethane class, in some cases it was found that powdery microcrystalline samples have a sign opposite to that for the same dye layers deposited from solutions. Thus, for example, crystal violet, which in a microcrystalline layer in air gave the sign + for the light current carriers ([3]), showed in air the sign − for a mirror layer of the same dye ([4], [13], [14]). On the other hand, a dye of the same class, brilliant green, which in air in microcrystalline powder gave the sign + (^{13}), in a mirror film invariably showed the sign − (^{14}). A discrepancy in the thermoe.m.f. signs for crystalline violet in air was also observed by Nelson (^{9}). In their latest note, Petrucello and Nelson (^{15}) came to the conclusion that evacuation of air affects the sign of the thermoe.m.f. of triphenylmethane dyes. For one and the same layer of crystal violet, the sign of the thermoe.m.f. in air is +, whereas in vacuum it is −.

To clarify the question of which factors are decisive for the sign of photocurrent carriers, the following experiments were set up in preparing dye samples.

The spectral distribution of the photoelectric sensitivity of dye layers and the sign of the light current carriers in them were determined by the methods of static (^{1}-^{5}) and dynamic (^{5}, ^{6}, ^{16}) capacitors. The sign of the dark current carriers was determined from the thermoelectric effect. Dyes manufactured by National Aniline Division were used.

Layers of brilliant green deposited from a saturated solution in ethanol onto a mica, glass, or platinized substrate have a mirror-like surface, selectively reflecting spectrally, and are dark green in transmitted light. In air the sign of the light carriers, determined by the capacitor and contact-potential methods, is negative in these layers. Upon prolonged pumping in vacuum at 10^{-5} mm Hg at 20°, the photo-e.m.f. of the mirror layer increases in absolute value, but its negative sign does not change. In the spectral distribution of the capacitor photo-e.m.f. of such a layer (Fig. 1, 1) there are distinct maxima at 640 and 590 nm, coinciding with the absorption spectrum (curve 3), which resembles the absorption spectrum of a concentrated solution.

However, if, with the specimen in vacuum, deoxygenated ethanol vapor ($p \sim 10$ mm Hg) is admitted into the vessel for 20–30 min and then pumped out, a sharp change in the appearance of the layer occurs. Its color in transmitted light changes from dark green to blue, and the surface changes from mirror-like to matte and scattering. When the layer is observed under a microscope at a magnification of 100–400×, one sees the formation of many individual particles of microcrystallites of the order of 10 μ in size. The sign of the photocurrent carriers then becomes positive, and in the spectral distribution of the photo-e.m.f. broadened maxima are observed at 690, 620, and 560 nm (curve 2), reproducing the change in the absorption spectrum of the layer (curve 4). Admission of air now increases the photo-e.m.f. by 40–50%, but for some "blue" layers the maximum photo-e.m.f. is observed already at an air pressure of the order of 0.1–1 mm Hg. The same changes in the sign and in the spectral distribution of the photo-e.m.f. occur if the mirror layers are treated in ethanol vapor not under vacuum conditions but simply in air.

Fig. 1. Spectrum of the photo-e.m.f. (1, 2) and absorption spectrum (3, 4) of a layer of brilliant green deposited from an ethanolic solution: 1, 3 —mirror layer in air; 2, 4 —matte layer after treatment of the mirror layer with ethanol vapor in vacuum.

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Figure 1: Fig. 1. Spectrum of the photo-e.m.f. (1, 2) and absorption spectrum (3, 4) of a layer of brilliant green deposited from an ethanolic solution: 1, 3 —mirror layer in air; 2, 4 —matte layer after treatment of the mirror layer with ethanol vapor in vacuum.

Fig. 2

Figure 2: Fig. 2

An analogous picture is observed for the contact photopotential of the same dye. The change in the potential of mirror layers both in air and in vacuum toward a positive surface charge indicates the formation of electrons and their diffusion into the interior under illumination. In vacuum the change in the contact potential under illumination is greater than in the presence of air. After admission of ethanol vapor the sign of the contact photopotential changes to the opposite one.

Microcrystalline precipitates of brilliant green, obtained by repeated recrystallization from an ethanolic solution, likewise exhibit a positive sign of the photocurrent carrier, as does the original dye powder.

The sign of the charge of the dark current carriers in mirror layers, determined from the thermo-e.m.f., is also negative. After treatment of these layers with ethanol vapor the sign of the thermo-e.m.f., like the signs of the capacitor photo-e.m.f. and the contact photopotential, changed to the opposite one in complete accordance–

correspondence with the signs of the light carrier. The results did not depend on whether the measurements were made in air or in vacuum. A change in the sign of the photovoltage carriers depending on the method of applying the dye was also found by us for crystal violet, malachite green, and auramine O, which belong to the same class of di- and triphenylmethane dyes. The initial microcrystalline powder of crystal

Fig. 2. Spectrum of the photo-emf of crystal violet in vacuum: **1** —crystalline powder; **2** —mirror-like layer deposited from an ethanolic solution; **3** —the same layer 2 in vacuum after contact with ethanol vapor

Fig. 3. Spectral dependence of the absolute magnitude of the change in the

Fig. 3

Figure 3: Fig. 3

contact potential of crystal violet in vacuum: **1** —mirror-like layer; **2** —microcrystalline matte layer

violet in air, in our apparatus, exhibited a positive carrier sign (Fig. 2, 1). In contrast to microcrystals, mirror-like layers of this dye, deposited on insulating substrates from concentrated solutions in ethanol at 20°, exhibited in air low sensitivity and a negative carrier sign. Experiments showed that the properties of mirror-like layers of crystal violet are strongly influenced by the rate of evaporation of the solution, the temperature of the substrate, the pressure and humidity of the air, and also the surrounding vapors and gases. When the air is pumped out to 10^{-5} mm Hg, the negative carrier sign in good mirror-like layers is retained, and the sensitivity of the layer increases by one or two orders of magnitude. It is noteworthy that mirror-like layers, when exposed to ethanol vapor, show a rapid change of sign to positive and a change in spectral sensitivity (Figs. 2, 3). After these layers are treated with ethanol vapor in vacuum, the positive sign and the spectral distribution of the photo-emf do not change during prolonged pumping in vacuum, nor when the layer is brought out into air. A similar change in the sign of the photovoltage carrier occurs if the mirror-like layers are treated in ethanol vapor simply in air.

Figure 3 gives the spectral curves for the change in the absolute magnitude of the contact potential under illumination for layers of crystal violet with n-conductivity (curve 1) and with p-conductivity (curve 2). The signs of the change $\Delta K\Pi_L$ in the first and second cases are opposite.

For malachite green, analogous results were obtained. The sign of the photovoltage carrier and the spectral distribution of the photo-emf in layers of auramine O also depend on the state of aggregation of the dye. Usually, microcrystalline layers of this dye in air show a small sensitivity, and the photovoltage carriers in them, in air and in vacuum, are positive charges.

By contrast, mirror-like layers obtained by sublimation in vacuum have carriers of negative sign (Fig. 4, 1). Amorphous layers of auramine O, when brought out into air, rapidly transform into the form of microcrystals and change the carrier sign to positive (Fig. 4, 2).

It should be noted that similar changes in the absorption spectra for mirror and crystalline layers of this dye were previously observed by Lyzina and Vartanyan (17).

Thus, in mirror layers of the di- and triphenylmethane dyes studied, the light and dark current carriers in air and in vacuum are electrons. The same layers, transformed by adsorption of polar molecules into an aggregate of microcrystals, exhibit hole conductivity, which, as in the original microcrystalline powders, is preserved not only in air but also in vacuum. Evidently, contact of the mirror layers with vapors of water or alcohol causes their rapid recrystallization into a stable form with carriers of the opposite sign. An analogous reversal of sign was observed by us for metal-free phthalocyanine (11). Adsorption of polar gases and vapors on a dye can lead not only to a change in the form of aggregation,

Fig. 4. Spectrum of photo-e.m.f. of auramine O in vacuum: 1 —mirror layer, sublimed in vacuum; 2 —the same layer after exposure to air (microcrystals)

Figure 4: Fig. 4. Spectrum of photo-e.m.f. of auramine O in vacuum: 1 —mirror layer, sublimed in vacuum; 2 —the same layer after exposure to air (microcrystals)

but also to the creation of impurity levels both in the bulk and on the surface of the dye layer. In the case of compact mirror layers, the role of the dye surface interacting with the surrounding atmosphere, relative to its volume, is reduced to a minimum. Therefore the negative sign of the photocurrent carrier, inherent in the dye itself, is preserved also in air. In the formation of microcrystals, in which the dye molecules are apparently packed less densely and the surface is also more developed, the possibility is created for molecules capable of capturing electrons to penetrate into the lattice. As a result, hole conductivity appears in the microcrystalline layers, even under good-vacuum conditions.

Fig. 4. Spectrum of the photo-e.m.f. of auramine O in vacuum: **1** —mirror layer, sublimed in vacuum; **2** —the same layer after exposure to air (microcrystals)

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Note: Figure translations are in progress. See original paper for figures.