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Abstract

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ON THE QUESTION OF THE BARRIER PHOTO-EMF OF PHOTOCELLS WITH DYES

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Noddack and Meyer ($^{1-3}$) investigated the appearance of a photo-emf under "longitudinal" illumination of dye layers deposited on the surface of a massive metallic electrode and pressed against a semitransparent electrode. The layers were applied by precipitating dyes from alcoholic solutions and were illuminated in air with visible light. The presence of rectifying properties in the photocells led the authors to the conclusion that the photo-emf is of barrier origin. Since, when the air was pumped out (to 5 mm), the rectification and the photo-emf almost completely disappeared, Noddack and Meyer concluded that a film of adsorbed gas plays an essential role in the formation of the barrier layer. In the authors' opinion, the barrier layer is formed at the natural (non-pressed) contact of the dye with the metallic electrode. The sign of the photo-emf, determined from the sign of the photopotential at the back electrode, since the photo-emf was considered to be back-wall, was negative for almost all the dyes investigated.

As our experiments have shown*, if a dye layer precipitated from solution onto a quartz surface, on which platinum electrodes had previously been applied, is illuminated in air with a light probe at one of the electrodes, then even under "transverse" illumination a photo-emf is observed. For the majority of the dyes we investigated, however, the sign of the photo-emf was positive. Since the contacts of the dye with the electrodes were ohmic, the appearance of the photo-emf could not be attributed to a barrier photoeffect. From the properties of the photo-emf and the conditions of its appearance we concluded that we are dealing with a photoelectrochemical phenomenon, in general outline analogous to the Becquerel photovoltaic effect in dye layers immersed in electrolyte solutions (^{4}). In this connection, we carried out experiments to elucidate the role of the barrier layer in photocells with "longitudinal" illumination.

In contrast to the photocell of Noddack and Meyer (^{1}), in our photocell semitransparent metallic layers (Pt, Au, Rh), deposited on quartz plates, were used as both the front and the back electrodes. Rearranging the plates in the photocell made it possible to study the photo-emf under illumination of both the pressed and the natural contact of the dye with the electrodes. The thickness of the layers deposited on the electrodes by precipitation of dyes from alcoholic solutions was of the order of 30–50 mC . We shall distinguish photocells in which

Fig. 1

Figure 1: Fig. 1

the dye layer is deposited either only on the front electrode (type I), or only on the back electrode (type II), or on both electrodes (type III)**. The photocell was illuminated with visible with light from an incandescent lamp of 300 or 1000 watts. To measure the photo-emf (E_∞), a dc amplifier with an input resistance $R_{\text{in}} = 10^8$ ohms was used. E_∞ was determined from the voltage produced by the photoelement across a resistance $R_{\text{in}} \gg R$, where R is the internal resistance of the photoelement. The voltage sensitivity of the circuit was 10^{-4} V/mm. The short-circuit current (I_0) was measured with a galvanometer having a sensitivity of 10^{-9} A/mm.

For detailed investigation, pinacyanol, orthochrome T, and crystal violet were selected. At an illuminance of about 1000 lux, E_∞ often reaches 0.1-0.2 V. The time required for establishment of the stationary photo-emf at this illuminance was of the order of several seconds or tens of seconds; at 10 lux this time was measured in minutes.

Fig. 1. Dependence of E_∞ (1), I_0 (2), and R (3) on the illumination intensity: 1 $-E_\infty$, 2 $-I_0$, 3 $-R$ ($L = 100$ corresponds to an illuminance of about 1000 lux)

Figure 1 shows typical dependences of E_∞, I_0, and R on the illuminance L. The dependence of E_∞ on L is described by the equality $E_\infty = A \ln(1+BL)$, where A and B are constants. The dependence of I_0 on L, over an illuminance-variation interval of $1 : 100$, is satisfactorily approximated by the equation $I = kL^n$, in which n usually has values from 0.4 to 0.8. Measurements with interference filters showed that the maxima of E and I_0 approximately coincide with the absorption maxima of the dyes in the solid state.

Figure 2 gives the current-voltage characteristics of the dark current and photocurrent for a type I photoelement with pinacyanol (curves 1 and 2). Curve 1 indicates the presence of a blocking layer. Curve 2 shows that the photocurrent in the forward direction increases with increasing voltage, tending toward saturation, while in the blocking direction it decreases to zero.

From the current-voltage characteristic of the dark current for a type II photoelement (curve 3), obtained from a type I photoelement by interchanging the electrodes, it follows that the direction which in the type I photoelement was forward has become blocking in this photoelement, and vice versa. Meanwhile the photocurrent (curve 4) flows in the former, but now blocking, direction.

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* The work has been submitted for publication in the *Journal of Physical Chemistry.*

** Noddack and Meyer studied the photo-emf on type II photocells.

A type III photoelement, obtained from the former type I photoelement by replacing the rear electrode (not coated with dye) with another electrode, but one coated with dye, exhibits no rectifying properties; moreover, the dark current at small voltages obeys Ohm' s law (curve 5). This result definitely indicates the absence of a blocking layer in it, and not compensation of the action of two blocking layers, as might have been supposed. This is also indicated by the fact that the resistance of a type III photoelement is several times smaller than the resistances of each of the type I and II photoelements obtained from it. The presence of a blocking layer in the latter and its absence in a type III photoelement means that the effective blocking layer is formed at the pressure contact of the dye with the metal electrode, which is absent in the type III photoelement. It is noteworthy that, for all three types of photoelements in which one and the same dye layer was illuminated, not only is the direction of the photocurrent preserved (curves 2, 4, and 6), but the magnitude of the photo-emf (E_∞) also turns out to be almost the same.

These results, which are also valid for photocells with orthochrome T and crystalline violet, are difficult to reconcile with the idea of the barrier nature of the photo-emf. A comparative study of photocells of types I, II, and III shows that there is no causal connection between the photo-emf and the blocking layer, since neither the position of the latter relative to the illuminated electrode, nor its presence or absence (see the photocell diagrams in Fig. 2), affects the direction of the photocurrent or the magnitude of the photo-emf. A photocell with a dye layer is regarded by us as a source of non-barrier photo-emf connected in series with a rectifier. The action of the latter is manifested only in the form of the current-voltage dependences of the dark current and photocurrent.

The structure of the blocking layer and the mechanism of rectification at the dye—metal contact are not yet clear. It can only be stated that rectification occurs at an imperfect pressure contact of the dye with the metallic electrode and under conditions in which the conductivity of the dye layers is practically entirely electrolytic.* It is possible that the presence of a film of adsorbed gas also plays a substantial role.

Retention of the direction of the photocurrent for photocells of types I, II, and III means that the photo-emf in all three cases is a transfer emf. The occurrence of the photo-emf is due exclusively to the asymmetry of illumination of the two electrodes and does not depend on the kind of contact (pressure or natural) or on the material of the electrodes. With pinacyanol, orthochrome T, eosin, erythrosin, trypaflavin, fuchsin, Bengal rose, and some other dyes, the photopotential at the front electrode was positive, and only with crystalline violet, methylene blue, and phenosafranine was a negative photopotential observed. These results agree with the results obtained under transverse illumination of the layers.

Fig. 2. Current-voltage dependences of the dark current and photocurrent for photocells of types I, II, and III with pinacyanol: **1, 3, 5** —dark current; **2, 4, 6** —photocurrent. —electrodes, K —dye layer, —blocking layer. Along

the abscissa axes is plotted the potential of the external voltage at the front electrode.

It should, however, be noted that the positive photo-emf of photocells with pinacyanol and orthochrome T, at illuminances of the order of 2000–3000 lux, begins to decrease with further increase in illuminance. Pumping out the air causes a change in the sign of the photo-emf. At intermediate stages of pumping, the photocells show a positive photo-emf at low illuminances and a negative one at strong illuminances. The negative photo-emf of photocells with crystalline violet increases upon pumping

* The presence of moisture in layers of salt-like dyes leads to the appearance in them of electrolytic conductivity (4). This also explains the unusually high conductivity of the layers of these dyes in air. After thorough evacuation of the photocells, their conductivity decreases by a factor of 10^2–10^4 and ceases to depend on the direction of the applied field.

by several times*. Such behavior of photocells during evacuation may be understood if it is assumed that, under illumination in air, there is a superposition of two photo-emfs of opposite sign: a positive photo-emf, for the occurrence of which the presence of oxygen and, possibly, moisture is necessary, and a negative photo-emf, the observation of which is favored by a high level of illumination and the removal of oxygen (air). The occurrence of the positive photo-emf is associated with photooxidation of dyes in the presence of oxygen. The negative photo-emf probably has a purely photoelectric origin and is connected, for example, with the diffusion of light-generated current carriers. The diffusion photo-emf of powders of a number of dyes, in particular pinacyanol, has already been investigated by Pushcheiko ([5,6]), who used the capacitor method for its observation. Under the conditions of our experiments the dye is in contact with metallic electrodes, and therefore the phenomenon of diffusion photo-emf may be more complicated because of the influence of contact fields.

It is probable that there are also dyes for which the signs of the photo-emfs due to photoelectrochemical and photoelectric processes will be opposite, as well as dyes for which these photo-emfs will add rather than subtract, as occurs for pinacyanol, orthochrome T, and crystal violet.

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REFERENCES CITED

[1] W. Noddack, H. Meier, *Zs. Elektrochem.*, **57**, 691 (1953).
[2] H. Meier, *Zs. Wissensch. Photogr.*, **2**, 50, 301 (1955).
[3] H. Meier, *Zs. Elektrochem.*, **59**, 1029 (1955).
[4] A. N. Terenin, *Photochemistry of Dyes*, Izd. AN SSSR, 1947, p. 319.
[5] E. Pushcheiko, *DAN*, **59**, 471 (1948).
[6] E. K. Pushcheiko, *ZhFKh*, **22**, 1172 (1948).

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* With prolonged evacuation, the negative photo-emf of pinacyanol, orthochrome T, and crystal violet also begins to decrease. This decrease, however, if not too great, is to a considerable extent apparent and is due to an increase in the resistance of the elements by 10^3-10^4 times as a result of the removal of moisture and solvent residues. As a result, the condition $R_{\text{in}} \gg R$ is violated.

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