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Abstract

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PHYSICS

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KINETICS OF THE PHOTOCONDUCTIVITY OF PHTHALOCYANINES

(Presented by Academician A. N. Terenin, 1 II 1960)

The semiconductor properties of synthetic pigments—phthalocyanines—have been the subject of investigation by a number of authors ($^{1-9}$). Interest in clarifying the nature of conductivity and photoconductivity in these compounds is due to the fact that phthalocyanines are close analogues of natural pigments—chlorophyll and hemin. Most authors measured the relaxation of the photoconductivity of phthalocyanines chiefly at late stages of the rise and decay of the photocurrent (above 10^{-2} sec.). The aim of the present work was to investigate the relaxation processes of the photoconductivity of phthalocyanines at the very earliest stages. The objects of study were layers, sublimed in high vacuum, of phthalocyanines containing copper and magnesium, as well as metal-free phthalocyanine. Layers of the pigments studied, with thicknesses from $0.1\,\mu$ to several microns, were deposited by sublimation in vacuum on quartz or mica substrates that had platinum or gold electrodes on their surface, separated by a gap of 1 mm. These electrodes were previously deposited on insulating substrates by cathode sputtering. A voltage of 100–300 V was applied between the electrodes. Like most organic dyes, the resistance of phthalocyanine layers was high and, when illuminated with undecomposed light from an SVDS mercury lamp, amounted to 10^{11}-10^{9} ohms.

The relaxation of the photoconductivity of these pigments was studied by the taumeter method (^{10}), which makes it possible to observe simultaneously on an oscillograph the entire course of the rise and decay of the photocurrent. The instrument made it possible to measure relaxation times from $5 \cdot 10^{-6}$ to 10^{-2} sec. With a slit width of 2 mm, the cutoff time corresponded to $4 \cdot 10^{-5}$ sec. Illumination was carried out with visible light from a mercury lamp (SVDSH-120), modulated at a frequency of about 100 Hz and isolated by means of a yellow ZhS12 light filter (2 mm). The illumination power ranged from 10^{-3} to 10^{-5} W/cm$^2 \cdot$sec. The illumination level at the photosensitive resistor under test was varied by a factor of 10–100 by means of a set of calibrated neutral light filters.

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Experiments were carried out both in air and under vacuum conditions, and also in the presence of various vapors and gases in the temperature range from -100 to $+150°$.

1. Investigation of the kinetics of photoconductivity showed that the processes of rise and decay of the photocurrent in essentially all phthalocyanines occur in the time interval from 10^{-5} to 10^{-2} sec.

Figure 1a presents oscillograms of the change in photocurrent with time for a sample of metal-free phthalocyanine in linear (A) and exponential (B) sweeps. It is evident from the curves that the kinetics of photoconductivity has a complex character. The rise curves in most cases are symmetric with the decay curves only at the initial stages. During illumination by a rectangular light pulse of duration 10^{-2} sec., the photoconductivity of metal-free phthalocyanine very rapidly reaches its stationary value. Along with low-inertia processes, there are observed

and the slower subsequent stages of the rise and decay of the photocurrent. In the case of metal-free phthalocyanine, the fraction of the slow inertial component is small—about 15-20% of the stationary value of the photocurrent.

Fig. 1. *a*—metal-free phthalocyanine in air at $+20°$, $\tau_{1\text{decay}} = 1.3 \cdot 10^{-5}$ sec., $\tau_{2\text{decay}} = 3 \cdot 10^{-3}$ sec.; *b*—copper phthalocyanine at $+20°$ in air, $\tau_{1\text{decay}} = 2 \cdot 10^{-5}$ sec., $\tau_{2\text{decay}} = 4 \cdot 10^{-3}$ sec.; *c*—same as *b*, after heating to 100° in air for 2 hours, $\tau_{1\text{decay}} = 5 \cdot 10^{-5}$ sec., $\tau_{2\text{decay}} = 1.2 \cdot 10^{-2}$ sec.

Fig. 2. *a*—magnesium phthalocyanine 1 in air at $+20°$, $\tau_{1\text{decay}} = 6 \cdot 10^{-6}$ sec., $\tau_{2\text{decay}} = 1.6 \cdot 10^{-2}$ sec.; *b*—magnesium phthalocyanine 2 in air at $+20°$ (freshly prepared), $\tau_{1\text{decay}} = 6 \cdot 10^{-6}$ sec., $\tau_{2\text{decay}} = 7 \cdot 10^{-3}$ sec.; *c*—layer 2 after adsorption of water vapor upon heating to $+100°$, $\tau_{1\text{decay}} = 6 \cdot 10^{-5}$ sec., $\tau_2 > 10^{-2}$ sec.

The processes of rise and decay of the photocurrent depend on the illumination level and, in general, do not fit a simple exponential dependence. Consideration of the photoconductivity kinetics of phthalocyanines in an exponential sweep makes it possible to reveal, in individual sections of the photocurrent decay, two exponents with short and long proper times of duration $\tau_{1\text{decay}} = 1.3 \cdot 10^{-5}$ sec. and $\tau_{2\text{decay}} = 3 \cdot 10^{-3}$ sec. (Fig. 1 Ba).

Fig. 3. 1—the oscillogram of the curve of rise and decay of the photocurrent of metal-free phthalocyanine; 2—decay of the photocurrent for curve 1 in the

Fig. 3

Figure 3: Fig. 3

Fig. 4. Instantaneous relaxation times for a magnesium phthalocyanine-2 layer in air

Figure 4: Fig. 4. Instantaneous relaxation times for a magnesium phthalocyanine-2 layer in air

coordinates $1/i_\phi - t$

To determine the form of the laws of rise and decay of the photocurrent for these objects, the photocurrent decay curves were plotted in the coordinates $1/i_\phi = f(t)$. For this purpose the oscillograms of the photocurrent were projected with an enlarger onto millimeter paper. In Fig. 3, for the same specimen of metal-free phthalocyanine as in Fig. 1, the photocurrent decay curves versus time are presented in the coordinates $i_\phi - t$ and $1/i_\phi - t$. From the curves presented it is evident that the decay of the photocurrent after cessation of illumination obeys a hyperbolic law, which indicates a bimolecular recombination process.

In studying the influence of various factors it was shown that evacuation of the air, as well as prolonged heating to +100° of phthalocyanine

without metal, both in air and under vacuum conditions, as well as in the presence of oxygen or water vapor, does not produce noticeable changes in the duration and character of the relaxation processes.

2. In the same Fig. 1 are shown oscillograms of the photocurrent in linear (A) and exponential (B) sweeps for a sample of copper phthalocyanine before (b) and after (c) heating the layer to +100° in oxygen (air). As with the curves for metal-free phthalocyanine, the rise and decay curves of the photocurrent for copper phthalocyanine proved to be asymmetric and, in the general case, nonexponential. With the aid of an exponential sweep, on individual portions of the decay curves it was possible to distinguish two components with short and long characteristic times.

Fig. 4. Instantaneous relaxation times for a magnesium phthalocyanine-2 layer in air

In contrast to metal-free phthalocyanine, layers of copper phthalocyanine after subsequent heating in air or oxygen (under vacuum conditions) appreciably increased their inertia. Thermal activation of copper phthalocyanine in air at +100° for 1-2 hours reduced the fraction of the fast component to 40% of the maximum value of the photocurrent, while the inertia of the slow component increased by a factor of 3 or more (Fig. 1).

It is indicative that under these conditions the relaxation time of the photocurrent changed sharply with the intensity of illumination, which apparently was caused by enhanced localization of electrons on oxygen trapping levels, increasing the duration of the recombination processes.

3. In contrast to sublimed layers of copper phthalocyanine and metal-free phthalocyanine, layers of magnesium phthalocyanine sublimed in high vacuum onto mica or quartz substrates in a considerable number of cases possessed an amorphous structure and extremely low photosensitivity. It turned out that the same layers of magnesium phthalocyanine, evaporated in vacuum but onto substrates with gold electrodes, heated to +150° (mica, quartz), had a crystalline structure and, in comparison with amorphous layers, exhibited a higher photoelectric sensitivity.

Figure 2 gives oscillograms of the rise and decay of the photocurrent in linear (A) and exponential (B) sweeps for two samples of crystalline magnesium phthalocyanine. From the curves presented it is seen that the processes of rise and decay of the photocurrent in the very initial regions have low inertia and have a duration of $6 \cdot 10^{-6}$ sec. Along with these very rapid processes of rise and decay of the photocurrent, slower subsequent components are also observed, with characteristic times beginning from 10^{-2} sec and longer. Experiments showed that the inertia of magnesium phthalocyanine layers subjected to prolonged exposure to moist air (oxygen), even at room temperature, increases appreciably. For example, Fig. 2 shows that in a magnesium phthalocyanine-2 layer, under the influence of moist air, the characteristic decay time of the short

the photocurrent component increases by a factor of 10 or more. When the illumination level is reduced by a factor of 5, the decay time of the short component increases to 10^{-4} sec. In this case, however, the character of the regularities themselves does not change.

Analysis of the decay curves by means of a plot of "instantaneous relaxation times" ([11]) showed that, as in copper phthalocyanine and metal-free phthalocyanine, the photocurrent decay process in the case of magnesium phthalocyanine also fits a simple hyperbolic dependence. Figure 4 gives the photocurrent decay curve for one of the magnesium phthalocyanine samples, measured by the "partial times" method with exponential sweep. The same figure gives the instantaneous relaxation time θ, which characterizes the time variation of the reciprocal of the logarithmic derivative of the photocurrent.

It should be noted that the photocurrent decay of phthalocyanines at later stages, from 10 sec to 5 min after cessation of illumination, according to the data of A. T. Vartanyan and I. A. Karpovich ([7]), also obeys the hyperbolic law well.

Analysis of the data obtained permits the following conclusions. The short-time course of photoelectric processes in solid layers of phthalocyanines over times of the order of 10^{-5} sec undoubtedly indicates the electronic nature of the observed phenomena. The decay of photoconductivity for all phthalocyanines has a recombination character. In general form, the photocurrent decay fits a simple hyperbolic dependence.

The pronounced dependence of the relaxation of photoconductivity in these pigments on the intensity of illumination in the presence of oxygen is apparently caused by localization of electrons at trapping levels, which increase the duration of recombination processes.

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