PHYSICAL CHEMISTRY

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. K. Putséiko

THE INFLUENCE OF ELECTRON-ACCEPTOR IMPURITIES ON THE OPTICAL AND PHOTOELECTRIC PROPERTIES OF MAGNESIUM PHTHALOCYANINE

(Presented by Academician A. N. Terenin, October 18, 1962)

In our previous works (1,2) it was shown that the state of aggregation of solid layers of magnesium phthalocyanine, as well as the treatment of these layers with certain solvents (ethanol, acetone), has a noticeable influence on the optical and photoelectric properties of this pigment.

In the present work, absorption and photoeffect spectra were investigated in amorphous and microcrystalline layers of magnesium phthalocyanine with electron-acceptor additives. The objects of investigation were layers of magnesium phthalocyanine sublimed in a vacuum of 10^{-5} mm Hg onto mica or quartz substrates, as well as layers of this pigment deposited from concentrated solutions in acetone, ether, and other solvents. The starting material was magnesium phthalocyanine powder synthesized at the Ivanovo Chemical-Technological Institute.*

The absorption spectra of the layers studied were measured on a Beckman quartz spectrophotometer with a microattachment described by us earlier in work (3). The shape and dimensions of the aggregated and crystalline particles were examined under a microscope at 600×, and also on X-ray diffraction patterns. The spectra of photoelectric sensitivity were measured by the photoconductivity method at constant voltage and constant illumination, and also by the capacitor method (4), which records the diffusion photo-emf arising on the plates of a capacitor under the action of modulated illumination.

The spectral distribution of the photo-emf and photoconductivity was determined with a single-prism glass monochromator in the wavelength interval 0.4–1.5 μ, with a spectral slit width of 1–5 mμ/mm. The spectral curves given below (in Figs. 2–4) are referred to equal incident monochromatic energy. The power of monochromatic illumination from an incandescent lamp beyond the output slit of the monochromator was 10^{-7}–10^{-4} W/cm^2. The photoconductivity and photo-emf spectra were measured within the range of a linear dependence of the photoresponse on the illumination intensity.

Absorption spectra of solid layers of magnesium phthalocyanine in different forms of aggregation

Experiments showed that layers of magnesium phthalocyanine sublimed in high vacuum (10^{-5} mm Hg) onto insulating substrates (mica, quartz) at room temperature, 20°, possess an amorphous structure. In the absorption spectra of these layers in the visible region two broad bands are observed, with maxima at 630 and 690 mμ (Fig. 1, 1). The conditions of evaporation, the substrate temperature, the air pressure, and a number of other factors have a noticeable influence on the state of aggregation of magnesium phthalocyanine during its sublimation, as was also observed for layers of metal-free phthalocyanine (5). A particularly distinct change—aggregation manifested itself when sublimation of the pigment was carried out onto substrates heated to 100–150° (mica, quartz), bearing on their surface a layer of evaporated metals—gold or platinum—separated by narrow gaps. Such layers of magnesium phthalocyanine in transmitted light exhibited a greenish-blue coloration and differed noticeably in color from the blue coloration of the same layers simultaneously sublimed onto clean dielectric substrates. Spectrally, this effect is manifested in the fact that in the absorption spectrum of a magnesium phthalocyanine layer with a blue-green coloration an additional, clearly expressed broad infrared absorption band is observed, with a maximum at 820 mμ (Fig. 1, 2). Similar changes in the absorption spectra were observed for the same layers of amorphous magnesium phthalocyanine after they had been treated with liquid solvents (immersion in liquid acetone, ether, and ethanol). As a result of such treatment, in the absorption spectrum of this layer there also appears a new infrared absorption band with a maximum at 820 mμ (Fig. 1, 3). The appearance of this long-wavelength absorption maximum was also found by us when layers of magnesium phthalocyanine were obtained by precipitating this pigment from a concentrated solution of acetone in air. The results obtained show that, irrespective of the method of treating the pigment, in the absorption spectra of magnesium phthalocyanine one and the same additional band invariably appears, with a maximum at 840–820 mμ. Apparently, this is caused by the formation in the layers of this pigment of one and the same aggregated form of the pigment—possibly crystalline, with inclusion of solvent molecules.

Fig. 1. Absorption spectra of thin films of magnesium phthalocyanine: 1—obtained at a substrate temperature of 20°; 2—the same, 150° (on a surface carrying gold electrodes); 3—obtained after treating layer 1 with liquid acetone.

Spectra of the photo-e.m.f. and photoconductivity of magnesium phthalocyanine in various forms of aggregation. Analogously to the absorp-

---

* The author expresses deep gratitude to V. F. Borodkin for providing the magnesium phthalocyanine.

Fig. 1. Absorption spectra of thin films of magnesium phthalocyanine: 1—obtained at a substrate temperature of 20°; 2—the same, 150° (on a surface carrying gold electrodes); 3—obtained after treating layer 1 with liquid acetone

Figure 1: Fig. 1. Absorption spectra of thin films of magnesium phthalocyanine: 1—obtained at a substrate temperature of 20°; 2—the same, 150° (on a surface carrying gold electrodes); 3—obtained after treating layer 1 with liquid acetone

Figure 2 and Figure 3: spectral distributions of photo-e.m.f.

Figure 2: Figure 2 and Figure 3: spectral distributions of photo-e.m.f.

tion spectra, the spectral distribution of the photoeffect in layers of magnesium phthalocyanine also depended on the state of aggregation and subsequent treatment of the pigment. Figure 2, 1 shows the photo-e.m.f. spectrum for an amorphous layer of magnesium phthalocyanine sublimed in vacuum, measured several minutes after the layer had been exposed to air. Such layers usually show low photosensitivity, and the carriers of the photocurrent in them are positive charges.

Experiments showed that thermal activation of the layer in water vapor under vacuum, or bringing this layer into contact with liquid solvents, not only increases the photoeffect but also promotes the formation of a new infrared photoeffect band with a maximum at 840 mμ (Fig. 2, 2). This is apparently due to the fact that, under such treatment, layers of magnesium phthalocyanine pass into another aggregated, more photosensitive state, with inclusion of water or solvent molecules (acetone, ethanol). Assuming that the change in the photoeffect spectra in these layers is also caused by the appearance of a new crystalline form of the pigment, we investigated the spectral distribution of the photoeffect in crystalline layers of this pigment. Prolonged heating for 5-6 hours at 300° of magnesium phthalocyanine layers in vacuum promotes, as is known,

to the formation of the crystalline β-form of the pigment. The experiments showed that the process of transition of the amorphous form of magnesium phthalocyanine into the crystalline β-form is accompanied not only by a significant increase in the pigment’ s sensitivity, but also by a shift of the main maximum of the photoeffect into the infrared region of the spectrum (Figs. 2, 3). However, upon prolonged storage in air this crystalline β-form of the pigment again passes into the amorphous form (Fig. 2, 4).

Fig. 2. Spectral distribution of the photo-e.m.f. in thin films of magnesium phthalocyanine obtained by sublimation in vacuum: **1**—at a substrate temperature of 20°; **2**—after treating layer 1 with liquid acetone; **3**—layer 1 after annealing in vacuum at 300° C for 5 h; **4**—the same layer 3 after storage in air.

Fig. 3. Spectral distribution of the photo-e.m.f. in thin films of magnesium phthalocyanine sublimed in vacuum, before (**1**) and after (**2**) activation with quinone from an ethanol solution.

Figure 4

Figure 3: Figure 4

A particularly distinct change in the photoeffect spectra is also observed when quinone molecules from dilute ethanol solutions are adsorbed onto the surface of amorphous layers of magnesium phthalocyanine. Such adsorption of quinone molecules, which possess electron-acceptor properties, not only modifies the spectral course of the photoeffect but also increases the sensitivity of the magnesium phthalocyanine layers by 2-3 orders of magnitude. For example, curves 1 and 2 in Fig. 3 show the photo-e.m.f. spectra for one and the same layer of magnesium phthalocyanine before and after repeated activation with quinone from an ethanol solution. From the curves presented it is evident that, under the influence of adsorbed quinone molecules, a new, sharply pronounced photoeffect band appears in the photo-e.m.f. spectrum, with a maximum at 840 mμ. At the same time, the sensitivity of the pigment increases up to 500-fold.

It is noteworthy that analogous effects are observed for layers of magnesium phthalocyanine deposited on photoresistor cells. Under these conditions the dark resistance of magnesium phthalocyanine in a thin layer—several hundredths of a micron thick, deposited by sublimation in vacuum onto platinum electrodes (with gaps of 0.1 mm)—at room tem-

At room temperature, it exhibits a high resistance of the order of 10^{10}–10^{12} ohms. Under the influence of humid air, with time (after several days) the conductivity of the layer increases sharply by 3-5 orders of magnitude. During this time the photosensitivity of the layer, i_ϕ/i_t, where i_ϕ is the photocurrent and i_t is the dark current, under illumination with light from an incandescent lamp decreases by 2-3 orders of magnitude. Experiments showed that pigment layers that had lost sensitivity restore it again upon deposition onto the surface of this pigment of electronegative quinone molecules from an ethanol solution. As a result of such activation, the dark resistance and photosensitivity of magnesium phthalocyanine increase by 3-5 and 2-3 orders of magnitude, respectively. At the same time, in the photoconductivity spectra an additional infrared photoeffect band is observed, shown in curves 1, 2, 3 of Fig. 4. It is also interesting to note the fact that the inertia of photoconductivity in these samples is noticeably reduced under the influence of adsorption of quinone molecules.

Fig. 4. Spectral distribution of the photoconductivity in a thin film of magnesium phthalocyanine, sublimed in vacuum and activated with quinone from an ethanol solution: after the first activation (1), the second (2), and the fourth (3)

The totality of the data obtained reveals the role of molecules of certain organic solvents (ethanol, acetone, ether), especially electronegative compounds (quinone), in the polymorphic transformations of magnesium phthalocyanine. The increase in photosensitivity of magnesium phthalocyanine containing a quinone impurity can be attributed to the formation of surface impurity centers on which electrons are fixed, while holes participate in conduction. The formation in layers of amorphous magnesium phthalocyanine of the crystalline β-form of the pigment or, possibly, of crystalline complexes of the pigment with inclusion of molecules of water, ethanol, oxygen, quinone, etc., not only favors a 100–1000-fold sensitization of the photoeffect, but also leads to the appearance of a new intense photoeffect band in the infrared region of the spectrum with a maximum at 840 mμ. The necessity of treating layers of magnesium phthalocyanine with compounds capable of bonding with magnesium phthalocyanine molecules in order to enhance the photoeffect shows that the magnesium atom creates rather deep traps for conduction electrons and that its blocking by these addends is necessary.

In conclusion, the author expresses deep gratitude to Acad. A. N. Terenin for his unfailing interest in the work and valuable advice.

Received
12 X 1962

CITED LITERATURE

1. E. K. Pucheiko, ZhFKh, **30**, 1019 (1956); J. Chim. Phys., **55**, 681 (1958).
2. E. K. Pucheiko, DAN, **124**, 796 (1959).
3. E. K. Pucheiko, Optika i spektroskopiya, **3**, 668 (1957).
4. E. K. Pucheiko, DAN, **59**, 471 (1948); Izv. AN SSSR, ser. fiz., **16**, 34 (1952).
5. V. S. Mylnikov, E. K. Pucheiko, Fiz. tverd. tela, **4**, 772 (1962).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.