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Abstract

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ON THE PHOTOCONDUCTIVITY OF VIOLANTHRONE AND PYRANTHRONE

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Akamatsu and Inokuchi found (^{1}) that layers of indanthrene dyes—violanthrone, isoviolanthrone, and pyranthrone—obtained by sublimation possess photoconductivity. By extrapolating a certain "linear" portion of the long-wavelength decline of the photoconductivity to its intersection with the axis of wave numbers, the authors determined the long-wavelength limits of the photoconductivity of these dyes and the corresponding optical activation energies E. For violanthrone and pyranthrone they obtained values of E equal, respectively, to 0.84 and 1.14 eV, which are in satisfactory agreement with the values of the thermal activation energy previously found by them (^{2}) (0.78 and 1.08 eV), and also with the long-wavelength absorption limits of the sublimed layers (^{1}). It should be noted, however, that the long-wavelength absorption band of layers of violanthrone, isoviolanthrone, and pyranthrone obtained by sublimation has a very large width, unusual even for the solid state of dyes, and an extremely weakly expressed structure. As a result, it is impossible to establish a direct connection between the absorption of sublimed layers and of solutions of these dyes. Meanwhile, the absorption of layers obtained by rubbing powders of violanthrone and pyranthrone onto a quartz surface is distinguished by sufficient selectivity (^{3}). The absorption band of such layers has maxima (Fig. 1, *1* and *2*) corresponding to the absorption maxima of solutions of the dyes in xylene, with the shift toward longer wavelengths usual for the solid state (^{4}), approximately by 40-45 mμ. In addition, it was found that the absorption spectrum of a layer sublimed once has a broader band and a less distinctly expressed structure than the spectrum of a layer obtained by rubbing; however, the similarity between these spectra is greater than between the spectra of layers obtained by rubbing and by repeated sublimation. Since dyes that do not change upon sublimation have absorption spectra that differ little from one another regardless of whether the layers are obtained by deposition of the dye from solution, by rubbing, or by sublimation (^{3}), it may be supposed that the repeated sublimation used by Akamatsu and Inokuchi for purifying the dyes caused certain irreversible structural changes.

In the present article, results are given of an investigation of the photoconductivity of layers obtained by rubbing powders of violanthrone (Indanthrene Dark Blue BO) and pyranthrone (Indanthrene Golden Orange G).

Fig. 1

Figure 1: Fig. 1

The investigation was carried out on an apparatus described in detail in the article (5). Layers with thicknesses from 0.1 to several microns were applied to a quartz "finger" having platinum electrodes separated by a gap of 1 mm. The photoconductivity was studied in vacuum, although experiments showed that the presence of air does not have a substantial influence on the results. The light source was a tungsten incandescent lamp with a power of 100 W. A mirror monochromator ISP-17A with glass optics was used for dispersion of the light. The distribution of energy by wavelengths was determined with the aid of a thermopile. Currents of the order of 10^{-13} A were measured with a direct-current amplifier.

Layers of violanthrone and pyranthrone obtained by rubbing possess appreciable dark conductivity, increasing with increasing temperature according to the law

$$\sigma = a \exp\left(-\frac{\varepsilon}{2kT}\right),$$

where ε is equal to 1.0 ± 0.05 and 1.15 ± 0.05 eV, respectively, for violanthrone and pyranthrone.

When the layers are illuminated, a steady photocurrent is established in a few seconds and decays almost as rapidly after illumination is stopped. Under prolonged illumination, a further increase of the photocurrent during illumination is often observed. After such prolonged illumination is stopped, the photocurrent falls rapidly at first, but a residual photocurrent is always observed, slowly decreasing with time. The results given below refer to the photocurrent that is established and decays within 3-5 sec. Under monochromatic illumination, the measured photocurrent was of the same order as the dark current.

Fig. 1. 1 –spectral absorption curve of a solid layer of violanthrone; 2 –the same for pyranthrone; 3 –spectral curve of the photosensitivity of a thin layer of violanthrone, $n = 0.9$; 4 –the same for pyranthrone, $n = 0.7$.

The photocurrent obeys Ohm' s law, at least in fields up to 4000 V/cm. The dependence of the photocurrent i_ϕ on the illumination intensity L is expressed by the relation $i_\phi = aL^n$, where a and n are constants. For the layers we investigated, the values of n were less than unity and, depending on the layer thickness and the illumination level, lay between 0.7 and 0.9. In the temperature interval from -40 to $+50^\circ$, the dependence of the photocurrent on temperature also follows the law

$$i_\phi = b \exp\left(-\frac{\varepsilon_\phi}{2kT}\right),$$

Fig. 2. Photoelectric straight lines: 1 –violanthrone, $n = 0.72$; 2 –pyranthrone, $n = 0.7$

Figure 2: Fig. 2. Photoelectric straight lines: 1 –violanthrone, $n = 0.72$; 2 –pyranthrone, $n = 0.7$

where for violanthrone $\varepsilon_\phi = 0.4$ eV.

Figure 1 (3 and 4) shows the spectral photosensitivity curves S of thin layers of violanthrone and pyranthrone. As the measure of photosensitivity we took the expression $i_\phi^{1/n}/L$, which takes into account the nonlinear dependence of the photocurrent on illumination intensity (^{6}). As is seen from Fig. 1, these curves are in good agreement with the absorption curves of solid layers. In the region of the long-wavelength decrease of photosensitivity there is a linear dependence between $\lg S$ and λ.

The photosensitivity curves shown in Fig. 1 cannot be compared with the curves obtained by Akamatu and Inokuchi (^{1}), if only because the absorption spectra of the layers in our experiments and in those of the authors mentioned are sharply different. In addition, the photosensitivity curves obtained by Akamatu and Inokuchi cover not the entire absorption band, but only its long-wavelength part, approximately from 640 to 1800 mμ. For a certain portion of this region they find a linear dependence between S and $1/\lambda$ and use it in determining the photoconductivity threshold. Quite apart from the fact that the extrapolation method used by Akamatu and Inokuchi for determining photoconductivity thresholds requires justification, the reality of linear sections on the photosensitivity curves of isoviolanthrone and pyranthrone appears doubtful.

To determine the optical activation energy, we used two independent methods that had already been employed in studies of inorganic photoconductors.

1. According to Moss[7], as the "long-wavelength limit" of photoconductivity one may take the wavelength at which the sensitivity falls to one-half of its value at the maximum immediately preceding the exponential decrease ($\lambda_{1/2}$). From curves 3 and 4 in Fig. 1 it follows that $\lambda_{1/2}$ is 720 mμ for violanthrone and 560 mμ for pyranthrone. The corresponding values of the optical activation energy $E_{\lambda_{1/2}}$ are, respectively, 1.71 and 2.2 eV.
2. The optical activation energy can also be determined by the method of "photoelectric straight lines." Lange and Schmidt[8] showed that, for the photocurrent arising when a photoconductor is illuminated by the total radiation of a black body having temperature T, the relation $i_\phi = AT^2 \exp(-E_\phi/kT)$ is satisfied, from which there follows a linear dependence between $\lg(i_\phi/T^2)$ and $1/T$. The slope of the straight line determines the magnitude of the optical activation energy E_ϕ.

Fig. 2. Photoelectric straight lines:
1 –violanthrone, $n = 0.72$; 2 –pyranthrone, $n = 0.7$

It was shown earlier[6] that for layers of one and the same dye, but with different values of n, the slope of the "photoelectric straight lines" depends on n, and therefore the values of E_ϕ found from such straight lines have no definite physical meaning. The slope of the straight lines proves to be independent of n and is determined exclusively by the nature of the dye if, instead of $\lg(i_\phi/T^2)$, one plots $\lg(i_\phi^{1/n}/T^2)$ on the ordinate axis. The "photoelectric straight lines" constructed with allowance for the "nonlinearity" of the photocurrent are shown in Fig. 2. The values of E_ϕ obtained from these straight lines, equal to 1.7 eV for violanthrone and 2.24 eV for pyranthrone, are in good agreement with the values of $E_{\lambda_{1/2}}$ and correspond to the beginning of the steep rise in the absorption of the dyes in the solid state. The latter fact may be used for a rough estimate of the optical activation energy from absorption curves.

The values of the optical activation energy obtained by us for violanthrone and pyranthrone are twice as large as the values found by Akamatu and Inokuchi[1]. Such a discrepancy is only partly due to the difference in the methods for determining this quantity. The main reason for the discrepancy is apparently the change in these dyes as a result of repeated sublimation.

From the fact that the obtained values of the optical activation energy are approximately twice as large as the values of the activation energy found from the temperature dependence of electrical conductivity, it still does not follow that the thermal activation energy differs significantly from the optical one, since the possibility is not excluded that the conductivity of the layers studied by us was not intrinsic but impurity conductivity.

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