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PVCz/HgS double layer structure for electrophotography

NAVNEET, P. K. C. PILLAI
Department of Physics, Indian Institute of Technology, New Delhi 110016, India

Xerographic characteristics of the double layer structure PVCz/HgS have been evaluated. These characteristics for the double layer have been compared with those for the single layer of HgS pigment and acrylonitrile–butadiene–styrene resin. Acceptance potential, fractional dark and photoinduced decrease, contrast potential, and relative spectral sensitivity are the most important characteristics studied. The double layer shows a maximum surface potential of 1632 V and 93% fractional decay of surface potential under illumination (intensity being 8.5 mW cm^{-2}), calculated 10 sec after the start of illumination. The spectral sensitivity is nearly panchromatic from 460 to 530 nm with a sensitivity peak at 585 nm in the visible region.

1. Introduction

Since the inception of electrophotography, amorphous selenium and ZnO binder layers are the two most widely studied electrophotographic materials. However, the discovery by Hoegl *et al.* [1] of photoconductivity in poly(n-vinyl carbazole), and afterwards its successful commercialization by the IBM corporation [2, 3], have provided a new avenue for exploration. Extensive laboratory efforts have been directed towards the development of new organic and inorganic compounds as potential electrophotographic materials. The basic requirement for an electrophotographic material is good charge retention and high sensitivity to visible radiations. Very few photoreceptors have equalled selenium and ZnO, with respect to the above requirements. The main drawback in organic materials has been the low efficiency of carrier generation and transport. Poly(n-vinyl carbazole), with and without trinitrofluorenone, has been investigated. Studies both in xerography [4–6] as well as photoconductivity [7–9] have been carried out on the above materials. Various multilayer structures have been tried, utilizing both organic and inorganic materials. Multilayer structures using poly(n-vinyl carbazole) as the charge storage layer with selenium or selenium–tellurium alloys as the photoactive layer have been described by Hayashi *et al.* [10]. According to Regensburger and Petruzzella [11], the multilayer plates would be comparable to single layer selenium and selenium–tellurium plates with respect to sensitivity and spectral response.

It has been shown in our earlier work [12] that the pigment–resin layer of red HgS, using acrylonitrile–butadiene–styrene as resin, shows a promising trend for xerographic applications. In the present study xerographic properties of a double layer consisting of an HgS pigment–resin layer overcoated with poly(n-vinyl carbazole) have been presented. The important xerographic features reported in this paper are: (a) acceptance potential, (b) fractional dark and photo-induced decay, (c) contrast potential, and (d) the spectral sensitivity curve. These properties are simultaneously compared for the double layer and HgS pigment–resin single layer. It was observed that the contrast potential and spectral sensitivity are enhanced by the double layer structure.

For brevity poly(n-vinyl carbazole), acrylonitrile–butadiene–styrene and tetrahydrofluorenone will be abbreviated as PVCz, ABS, and THF, respectively.

2. Experimental procedure

Red HgS was obtained from Riedel-de Heën AG Seelze-Hannover, Germany. The particle size of the pigment was about 2 μm. PVCz, obtained from

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Polysciences Inc., Warrington, was purified eight times by the precipitation technique. A solution of PVCz in benzene was allowed to fall drop by drop into methanol, which was continuously stirred. The ratio of benzene to methanol was at least 1:3 so that the monomer becomes dissolved in methanol, leaving behind the precipitated polymer. ABS was dissolved in a solution of benzene and acetone. HgS pigments were then milled with this solution to give a homogeneous dispersion of HgS pigments in the resin. The pigment to resin ratio was 70:30. The layers were cast on clean aluminium substrates. They were dried in the solvent atmosphere and traces of solvent were removed by keeping them inside an oven at 50° C for several hours. Once the layers were dry they were overcoated with a THF solution of PVCz. It is essential that the solvents of the base layer and the top layer do not mix together. The double layer structure thus obtained has a 50 μm HgS pigment–resin base layer, and a 10 μm overlayer of PVCz. Coating thickness was measured with a micrometer, accurate to 5 μm. All studies were conducted at a temperature of 30° C and 47% humidity atmospheric conditions.

The double layer was charged with the help of a scorotron [13] unit. The corona voltage, grid voltage and charging time were positive 7.5 kV, positive 1.5 kV and 60 sec, respectively. An especially designed hollow, cylindrical double walled vibrating probe [12], was used to measure the surface potential of the charged layer. It consisted of two coaxial aluminium cylinders separated by a teflon insulator which was stuffed between them. It was made to vibrate at a predetermined frequency. The voltage induced in the inner cylinder was monitored with the help of an a.c. microvoltmeter (Systronics, India). The outer cylinder was earthed. The sensitivity of the probe was 4.75 V. A 100 W tungsten filament lamp was used to illuminate the samples. The intensity of illumination was varied from 2.0 to 8.5 mW cm^{-2}. The wavelengths of the radiations were selected by using kodak narrow-band pass filters. The intensity of illumination was kept constant for spectral sensitivity studies. The corrections were made in order to take into account the number of photons not absorbed by the samples and the interparticle scattering of light, by taking the absorption spectra of the samples with the help of a spectrophotometer. The light reflected by the samples was measured for different wavelengths. Thus, the relative spectral sensitivity per unit intensity of illumination absorbed by the samples was calculated for various wavelengths. The intensity of light was measured by means of a thermopile.

3. Results and discussion

The observed surface potential discharge with time for the HgS pigment–resin single layer (SL) and the double layer (DL) of HgS overcoated by PVCz, in the dark, is shown in Fig 1. Photoinduced characteristics are given by Fig. 2, while Fig. 3 shows the contrast potential against exposure curves for different layers. Fig. 4 shows the plot of relative spectral sensitivity against wavelength of illuminating radiation.

3.1. Charge acceptance

Charge acceptance is the maximum charge that can be applied to and retained by a photoconductive layer. Shahin and Michael [14], using mass spectrometer techniques, have determined the types of ions generated in corona charging. During negative coronas, CO_3^- ions are the most dominant species. The exact nature of charging by CO_3^- ions on the polymer surface is not yet certain. It has been proposed [15, 16] that the polymer surface undergoes two chemical changes during the corona charging. One, the UV radiations in the corona break the carbon–carbon bond and supply sufficient energy for hydrogen atom rearrangement, thus forming double bonds ($>C{=}C<$). The other possibility is the formation of carbonyl ($>C{=}O$) groups, due to chemical combination of O_2, O^-, O_3 with double bonds. These bonds become the centres at which charge trapping may take place. These could be (a) on the molecular chains where charge is trapped at the atomic sites; (b) in a cluster of atoms where the electron is shared due to charge affinity of such groups of atoms; or (c) in both crystalline and amorphous regions of the polymers. Electron trapping may also take place by direct attachment of an electron to the oxygen molecule on the thin oxide film formed on the exposed polymer film. The activation energy of the electron is given by the electron affinity of molecular oxygen. According to Pillai and Chandrasekhar [17], the charging of the PVCz overlayer is due to trapping in the polycrystalline and amorphous regions of the polymer. The surface potential of the charged layers in the present case was observed to be 1632 V for both SL and DL layers.

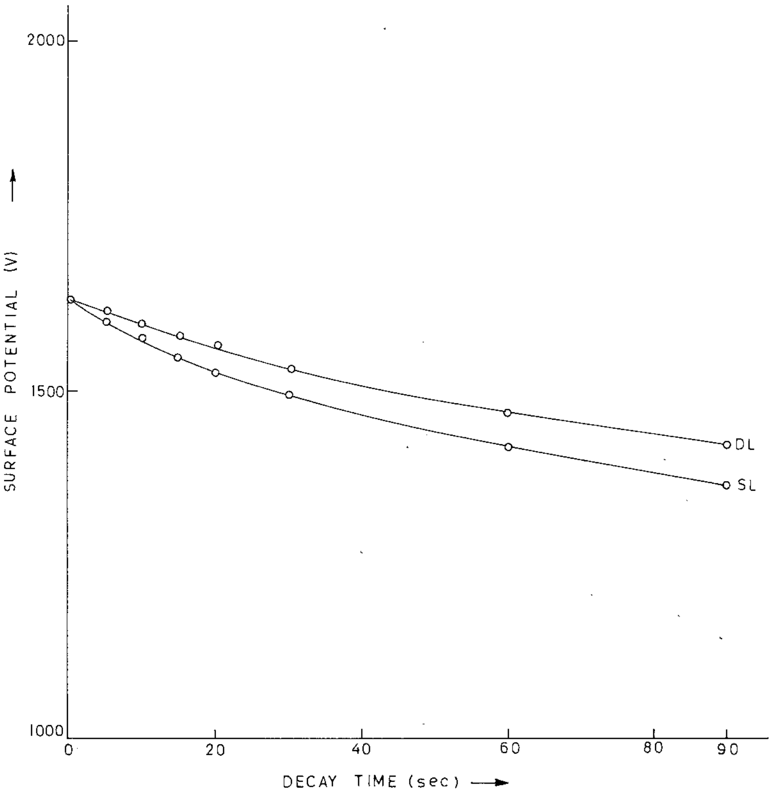

Figure 1 Dark decay characteristics for SL–single HgS binder layer, and DL–double layer of HgS overcoated with PVCz.

3.2. Dark decay characteristics

The decay of the charge takes place due to the detrapping of charges in the surface states. In the case of trapping at individual atomic sites on the main chain, detrapping would take place by individual atomic motions, whereas if trapped in a cluster of atoms, detrapping would take place by motion of the entire cluster of atoms. If the electron is trapped both in crystalline and amorphous regions, then the excitation is caused by main chain motion of the polymer. The fractional dark decrease in surface potential was 13% and 10% for SL and DL layers, respectively, calculated 60 sec after the charging of the layers. The dark

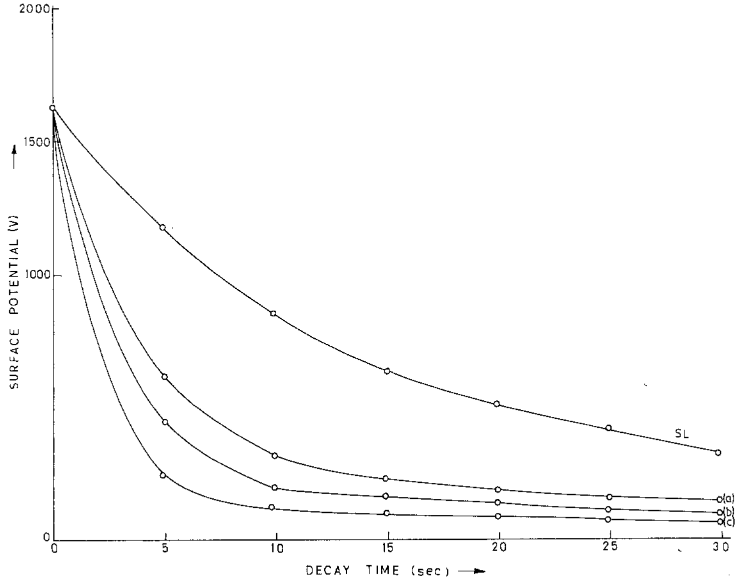

Figure 2 Photoinduced decay characteristics for SL–intensity of illumination is 8.5 mW cm^{-2}; and for DL–intensity of illumination is (a) 2.0 mW cm^{-2}, (b) 4.0 mW cm^{-2}, and (c) 8.5 mW cm^{-2}.

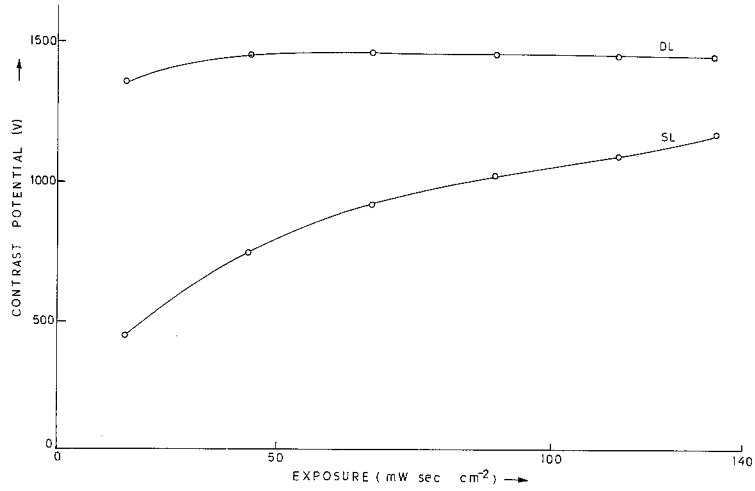

Figure 3 Contrast potential against exposure for SL and DL; intensity is 8.5 mW cm^{-2}.

decay rate of DL becomes slightly slower than that of SL (see Fig. 1).

3.3. Photoinduced characteristics

Photoexcitation in the DL increases substantially. Photoresponse in the multilayer structure is provided by photoexcitation in the HgS base layer and subsequent hole injection in the PVCz, since the PVCz layer is essentially transparent. The fractional light decay, calculated 10 sec after the start of illumination, was 47.7 and 92.9% for the SL and DL, respectively. The residual potential is fairly small for DL. It appears that the PVCz layer has provided more effective absorption of incident light. Fig. 2 shows the photoinduced decay of the DL for different intensities of illumination; (a) 2.0 mW cm^{-2}, (b) 4.0 mW cm^{-2}, (c) 8.5 mW cm^{-2}. For the SL, the incident intensity was 8.5 mW cm^{-2}.

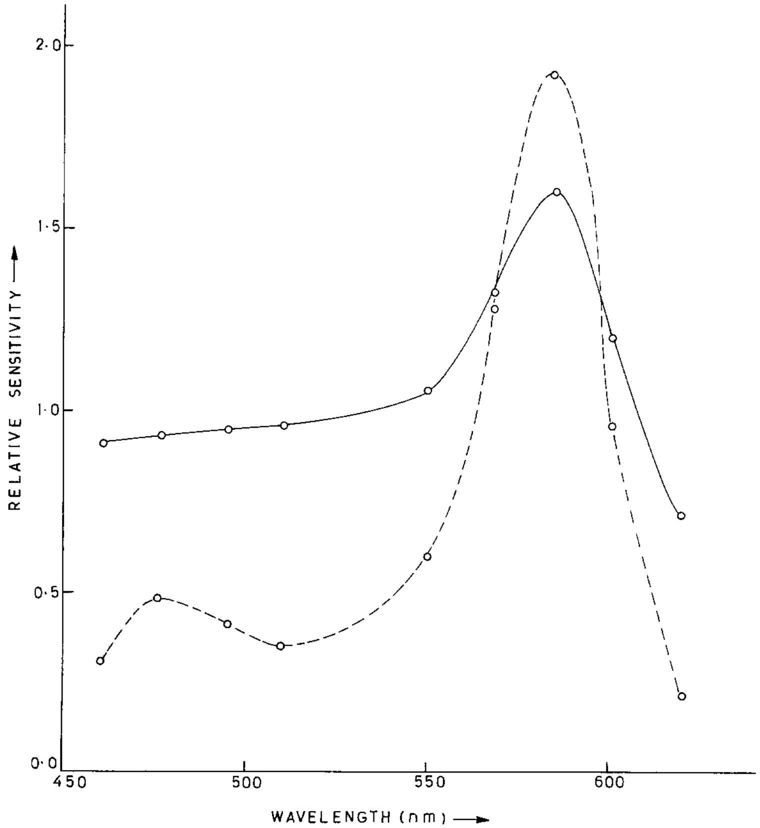

Figure 4 Relative spectral sensitivity curve; the dashed curve is for SL, and the line curve for DL.

3.4. Contrast potential

The difference in electrostatic potential between dark and light areas is known as the contrast potential. The contrast potential was observed to be as high as 1479 V for DL, calculated 10 sec after the start of illumination. For SL, on the other hand, its value was 732 V. The variation of contrast potential with exposure is shown in Fig. 3. It increases slowly with exposure for SL, but for DL it remains nearly uniform for a wide range of exposure.

3.5. Spectral response

The photosensitivity of a photoconductive layer is related to the rate of charge decay under illumination with light of a given intensity and given wavelength band. This rate, in turn, depends upon the quantum efficiency for exciting charge carriers to a conduction state, the mobility of charge carriers, the absorption of incident light within the layer, and upon the energy per photon as determined by the wavelength or range of wavelengths of the incident radiation. The effect of illumination by radiations of different wavelengths on the decay characteristics of the sample can be assessed quantitatively by the parameter, spectral sensitivity, given by

$$S_\lambda = \frac{C\Delta V_f}{I_\lambda t_h}$$

where C is the capacitance per unit area, ΔV_f is the change in surface potential at half-decay time, I_λ is the intensity of illumination absorbed by the sample, and t_h is the half-decay time. In the present case, the spectral sensitivity of the DL is enhanced in the visible region, as compared with the SL. The small peak at about 585 nm is due to HgS. PVCz is known to have nearly panchromatic response up to 600 nm in the visible region.

4. Conclusions

The double layer structure of PVCz/HgS has improved xerographic characteristics over the single HgS pigment–resin layer.

1. The double layer shows a high acceptance potential of 1632 V, which is highly stable. The fractional dark decay calculated 60 sec after charging is 10%.

2. The surface potential decays very fast on illumination of the layer. The fraction light decay calculated 10 sec after illumination starts is 93%, as compared with 48% for the single layer.

3. The contrast potential achieves a high value of 1480 V, 10 sec after the start of illumination. It remains uniform over the exposure range 45 to 135 mW sec cm^{-3}.

4. The spectral sensitivity curve shows two features. From 460 to 530 nm, the relative spectral sensitivity remains nearly panchromatic, and at 585 nm, there is a peak. Practical light sources, matching their emission spectra to that of the double layer spectral response, can be used for xerographic applications.

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