High field conduction in a double layer polymeric photoreceptor

P. K. C. Pillai and Shobha Chandrasekhar
Department of Physics, Indian Institute of Technology, New Delhi-110029, India
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Xerographic characteristics such as (i) maximum acceptance potential, (ii) quantum efficiency, (iii) reciprocity nature and (iv) dynamic law have been evaluated for a polymeric double layer system. The double layer consists of poly(9-vinyl anthracene) base on aluminium substrate, having an overlayer of 1.0 μm poly(n-vinyl carbazole). It was found to have good xerographic properties and can be used effectively in xerography.

INTRODUCTION

There is rapid progress in the utilization of polymers in industrial applications. Extensive research into applications of polymers is currently being undertaken but due to scarcity of photoconductive polymers, it has not been feasible to use polymers in photocopier systems. The most widely studied photoconductive polymer is poly(n-vinyl carbazole) and its complex with trinitrofluorenone (TNF). Studies both in xerography[1–3] and photoconductivity[4–6] have been carried out on the above materials. It has been shown in a previous communication[7] that poly(9-vinyl anthracene) is a good xerographic receptor. In the present study, xerographic properties of a double layer of poly(9-vinyl anthracene) overcoated with poly(n-vinyl carbazole) have been investigated.

The important xerographic features reported in this paper are: (i) maximum acceptance potential, (ii) contrast potential, i.e. the electrostatic pattern formed due to difference in surface potential in dark and illuminated areas, (iii) reciprocity nature and (iv) dynamic law.

It has been observed that certain characteristics such as quantum efficiency (η_λ), half-decay time (t_h) under illumination, and acceptance potential have been enhanced by the double layer structure of poly(9-vinyl anthracene) overcoated with poly(n-vinyl carbazole). This double layer system can therefore profitably be used in xerographic applications. It has been concluded that the charge carrier trapping takes place in the crystalline and amorphous regions of the polymer PVK which has high activation energy. The discharge process is found to be space charge limited in nature.

For brevity poly(9-vinyl anthracene) and poly(n-vinyl carbazole) will be abbreviated as P9VA and PVK respectively.

EXPERIMENTAL

PVK obtained from Luvican (170 BASF) was purified twelve times by the precipitation technique. In this method a solution of PVK in benzene was allowed to fall dropwise into a beaker containing methanol, and the contents were then stirred with an electrical stirrer (REMI, India). The ratio of benzene to methanol was at least 1:3 so that the polymer precipitated in methanol whereas monomer dissolves.

P9VA was dissolved in the tetrahydrofuranone (THF) and the solution was cast on an Al plate. This was then kept in a desiccator saturated with THF vapour, and allowed to dry for 24 h. After the P9VA layer was dry, it was further coated with a benzene solution of PVK. It is essential that the solvent of the base layer and the top layer do not mix with each other. The double layer thus formed has a photoconductive base of P9VA of 40 μm and an overlayer of u.v. sensitive PVK of 1.0 μm.

The double layer thus obtained was negatively corona charged with the help of a Scorotron unit (*Figure 1*). The surface potential was monitored with a transparent vibrating probe coupled to an a.c. microvoltmeter (Systronics, India). The discharge in the dark and under continuous illumination was recorded with the above set-up. The operating intensity range was (0.15–20) mW/cm^2. This was achieved with the help of neutral density filters (Optics Technology) and also by varying the distance between the source of light and the sample. Photoresponse in the entire visible range, i.e.

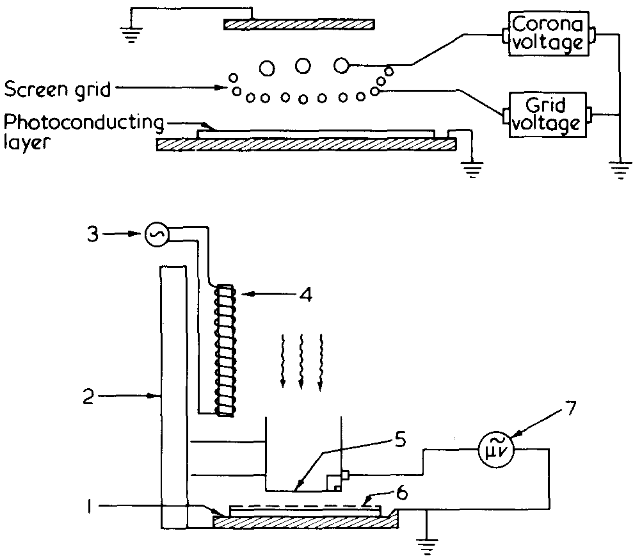

Figure 1 'Scorotron' charging unit: 1, Metal base; 2, Rigid support; 3, a.c. voltage; 4, Electromagnet; 5, Conducting glass; 6, Corona charged layer; 7, a.c. microvoltmeter

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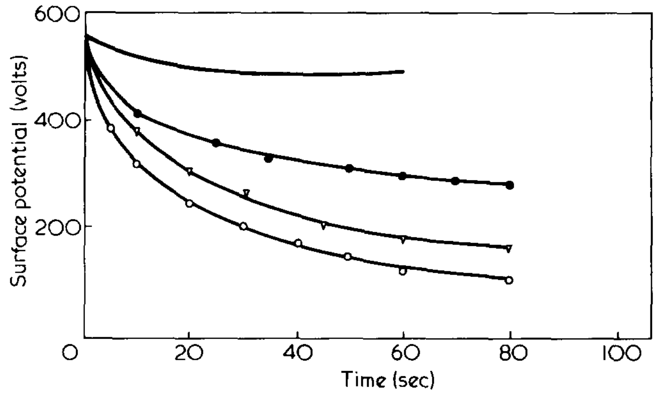

Figure 2 Decay of surface potential with time, —— (dark); ○, (20 mW/cm^2); ▽, (15.7 mW/cm^2) and ●, (0.15 mW/cm^2)

400–700 nm was scanned with the help of interference filters (Optics Technology). The charging parameters maintained in the present investigation were a.c. corona voltage at 6.0 kV, d.c. grid potential at 1.5 kV and charging time of 60 sec.

RESULTS AND DISCUSSIONS

Charge acceptance

The amount of surface charge that can be applied to and retained by a photoconductive layer is referred to as charge acceptance. Charge acceptance is not an independent property of the photoreceptor alone, but is dependent upon the corona charging parameters. The optimum charging conditions for the maximum charge acceptance by the P9VA:PVK double layer was found to be a.c. corona of 6.0 kV, d.c. grid potential of 1.5 kV and charging time of 60 sec.

Shahin[8] has shown that the predominant ion produced by negative corona is CO_3^-. The exact nature of the process of charging due to incidence of such ions on the polymer surface has not been properly investigated. However, several hypothetical explanations have been given. According to Baum *et al.*[9] charging might take place by transfer of electrons between the negative corona ion and the polymeric surface.

It has been proposed[10,11] that, when polymers are exposed to corona in air, at least two chemical changes take place in the polymer surface. One, there may be formation of double bonds (>C=C<). The u.v. light in the corona breaks the carbon–carbon bond and supplies sufficient energy for the H atom rearrangement thus forming bonds. The other possibility is the formation of carbonyl (>C=O) groups due to chemical combination of O_2, O^-, O_3 with double bonds. Consequently, carbonyl groups and double bonds become centres at which charge trapping may take place. These could be (a) on the molecular chains where the 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.

Another possible mechanism of polymeric surface getting corona charged is as follows. A thin oxide film is formed when the polymer film is exposed to air. When the polymer is corona charged, electron trapping takes place by direct attachment[12] of an electron to the oxygen molecule thus forming negative ion. The activation energy of the electron is given by the electron affinity of molecular oxygen.

Dark decay of surface charge

The decay of surface charge is due to detrapping caused by both lowering of trap depth by molecular motion and thermal excitation of the charge carriers.

In the case of charging by electron transfer between surface states and corona ions, dark discharge takes place by thermal release of the trapped electrons.

Further, 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 can take place by motion of the entire cluster of atoms. If the electron is trapped both in crystalline and amorphous regions, then excitation is caused by main chain motion of the polymer.

From *Figure 2* it is evident that the surface charge decays in dark from 560 V to 490 V in 29 sec and thereafter remains constant. The half-decay time, t_h, the time required for the surface charge potential to decay to half its initial magnitude is indeterminate in the present case. The surface potential becomes constant after decaying by 12.5%. Hence there is very good charge retention by the double layer system. Thus, the activation energy of most of the surface states or double bonds on carbonyl groups, which form the trapping centres on the polymeric surface, is much larger than the thermal energy ($=kT$). Hence those carriers which are trapped in centres having activation energy of the order of kT are thermally released, thus giving rise to initial surface potential decay, as shown in *Figure 2* (—). If we assume this to be true, then the majority of the carriers are trapped in the crystalline and amorphous regions of the polymer, which require larger energy of excitation. The initial decay of surface potential may be due to carriers trapped either in the individual atoms on the molecular chain or may be shared with few atoms such that the excitation energy is approximately kT.

Another plausible reason for the initial surface charge decay is that a small number of carriers are trapped in 'fast' states of the oxide layer. The oxide film which forms over the polymer film (due to exposure to air) has two types of surface states[13] viz. (i) 'fast' states, which have a high capture probability of carriers and are at the interface of the oxide and photoinsulating layers; (ii) 'slow' states having many orders of magnitude smaller capture probability than 'fast' states and existing on the oxide layer.

Baum *et al.*[9] have observed that the subsequent decay of surface potential after cessation of negative corona charging is more rapid in the areas which were exposed to corona light than in those regions which were shielded from corona light. This was not observed in the present case. Though PVK is u.v. sensitive, there has not been any appreciably faster decay of the double layer on negative corona charging. But, there have been reports of rapid dark discharge of PVK single layer, and quite appreciable surface charge dark decay of PVK:TNF::PVK double layer system. This implies that the potential barrier at the interface between the overlayer PVK and the base layer P9VA is appreciable to stop the flow of carriers in dark from PVK to P9VA. This is a highly advantageous feature of this xerographic layer since the electrostatic pattern on the photoreceptor can be retained for a considerable time.

Photodischarge

The surface potential was found to decay even after removal of illuminating radiation. This is characteristic of space-charge-perturbed discharge where the contrast poten-

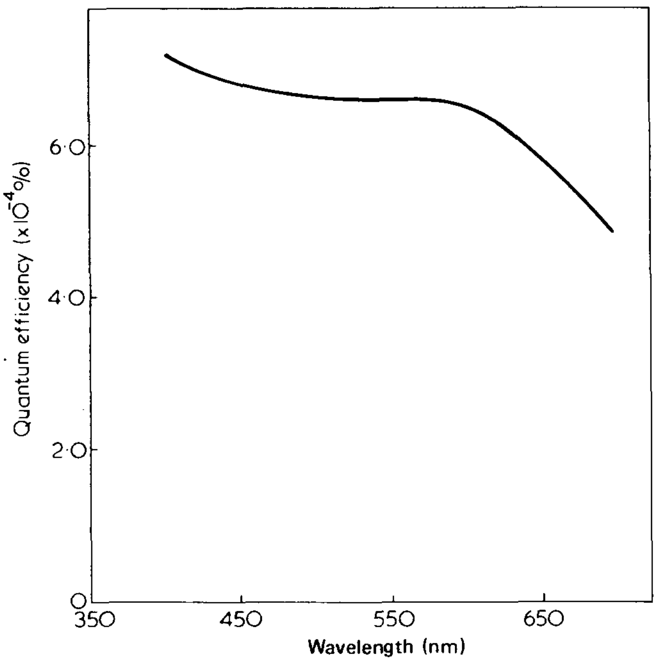

Figure 3 Variation of quantum efficiency with wavelength. (Intensity of illumination – kept at 100 $\mu W/cm^2$)

tial difference in the magnitude of surface potential in dark and under illumination, at any particular time – increases with time even after exposure was over until the growth is compensated by dark decay. Thus the mechanism of charge decay in the present system is space-charge-limited (*SCL*). In this mode of discharge (i.e. *SCL*) the transport properties of the carriers play a vital role.

From *Figure 2* we observe that the nature of discharge is *SCL* in the entire operating intensity range (0.157–20) mW/cm^2. When the intensity of illumination is sufficiently high so that all the surface charge is instantaneously injected into P9VA the hole current in P9VA will be space-charge-limited[7]. Even when the intensity is low the discharge current is space-charge-limited due to low mobility of holes in PVK[14].

Quantum efficiency

It is of interest to know the effectiveness of the incident photons on the surface charge, i.e. how many surface charges can be controlled by a single photon. In order to know this we determine a parameter, quantum efficiency, which is defined as:

$$\eta_\lambda = \frac{K \Delta V n_\lambda}{LI} \times 8.85 \times 10^{-6} (\%)$$

where K is the dielectric constant of the medium, ΔV the electrostatic contrast, n_λ is the energy carried per photon, L the thickness of the layer, and I the intensity of incident illumination. From *Figure 3* it is evident that the quantum efficiency of the P9VA:PVK system is approximately constant over the entire visible spectrum, when compared to that of amorphous Se[15] and ZnO[16].

Reciprocity law

A photoreceptor is said to be reciprocal if for any particular contrast potential the exposure required is independent of the intensity, i.e. a log (exposure) *versus* log (intensity) curve is a straight line parallel to the log(intensity) axis. In other words, different intensities of light reflected from various areas of the document should discharge the surface of the receptor in such a manner that the electrostatic pattern thus formed is a true replica of the optical contrast of the object.

Fridkin *et al.*[17] have proposed that the failure of the reciprocity law is due to the effect of thermal excitation of electrons from the trap levels. In very low intensity ranges the failure is attributed to the dominance of thermal excitation over optical excitation of electrons from traps. In low intensity ranges the failure of the reciprocity law is due to equal probability of thermal and optical transitions.

Hence from *Figure 4* it is found that the effect of the incident photons is not felt much. Since the probability of optical excitation is lower than thermal excitation in the intensity range (0.157–20) mW/cm^2, it is proposed that the electrons are trapped both in crystalline and amorphous regions of the polymer system. This is so, since detrapping in this case can be caused by main chain motion which requires a fairly large activation energy.

Failure of the reciprocity law can also be due to loss of carrier by either initial (geminate) or bimolecular recombinations. Thus the probability of detrapping by thermal or optical excitation (in the operating intensity range) is very low. This further strengthens the assumption that the electrons are trapped in the crystalline and amorphous regions of the polymer.

Dynamic law

It is that range of exposure in which the electrostatic contrast is a faithful reproduction of the optical contrast of the document. The optical density is inversely proportional to log (exposure). Now, for the dynamic law to be satisfied, the surface charge density should be proportional to the optical density, i.e. the surface charge density should be inversely proportional to log(exposure).

Hence graphically, dynamic law is defined as that range of exposure in which the surface potential *versus* log(exposure) is linear with slope of –1.0.

In the present case (P9VA:PVK) the dynamic law is obeyed (see *Figure 5*).

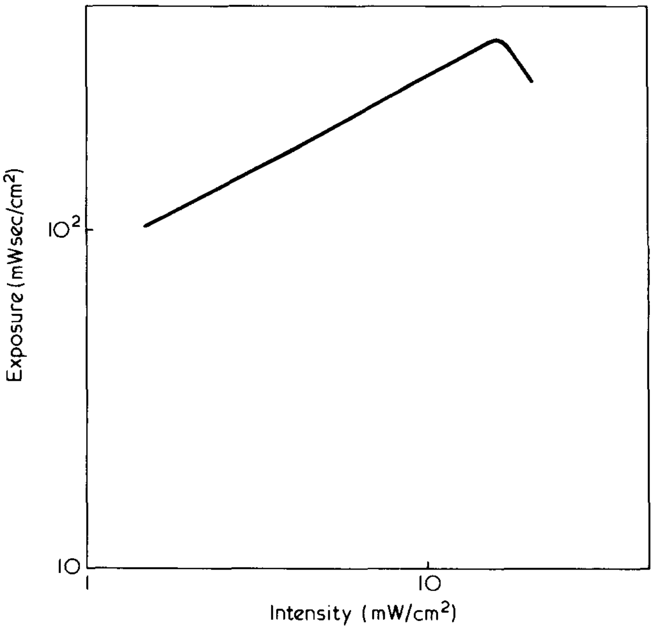

Figure 4 Reciprocity law curve of the sample

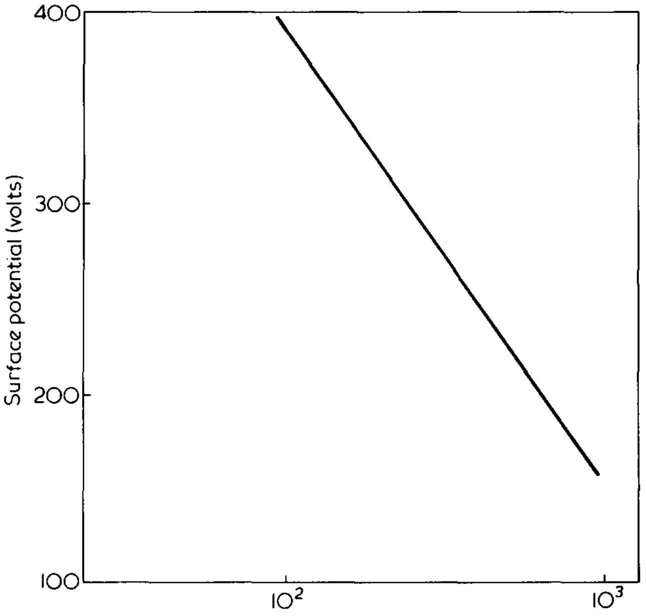

Figure 5 Dynamic law

CONCLUSIONS

From the present investigation, it has been concluded that:

(1) The double layer system of P9VA:PVK has improved the quantum efficiency and also the half-decay time, t_h, under illumination. There has not been considerable increase in the initial surface potential of the system. Since t_h in illumination is of the order of seconds, it can be efficiently used in short-exposure-time photocopier systems.

(2) The charging of the PVK overlayer is due to trapping in the polycrystalline and amorphous regions of the polymer.

(3) Due to high charge retention, it can be used very advantageously in photocopiers where the time lag between exposure and development is quite large, such as in manually operated machines.

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