Electrophotographic characteristics of pure and sensitized poly(*N*-vinyl carbazole)

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The electrophotographic characteristics of poly(*N*-vinyl carbazole) (PVK) are studied with reference to its purification and sensitization. PVK obtained after 12 cycles of purificiation gives best results. Photosensitivity of PVK is found to increase by doping with 2, 4, 7-trinitro-9-fluorenone (TNF). Further improvements in the electrophotographic characteristics are achieved by forming a double layer structure consisting of a thin PVK:TNF layer coated over a relatively thicker PVK layer

INTRODUCTION

Poly(N-vinyl carbazole) (PVK) is observed to be one of the best photoconducting polymers for electrophotographic applications[1–4]. The photoconductivity of commercial grade PVK is very low due to the presence of vinylcarbazole, anthracene and other monomeric impurities. These impurities can be removed by dissolving PVK in benzene and reprecipitating in methanol[5].

Although the maximum sensitivity of purified PVK lies in the ultraviolet region, its response may be extended to visible region by various sensitizing techniques[6–8]. Studies on PVK-acceptor dye complexes have shown that 2,4,7-trinitro-9-fluorenone incorporated in 1:1 molar ratio provides the best electrophotographic results[9].

When PVK:TNF photoreceptors are charged and exposed to light, the charge carriers are generated uniformly in the layer due to its small absorption coefficient. It has been found from the photoconductivity studies that conduction is dominated by holes[10]. Negative space charge is generated along with the generation of holes, and then, long time is necessary for the dissipation of this negative space charge. This disadvantage can, however, be overcome by the formation of a double layer structure, consisting of a thick PVK layer for carrier transport coated on a conducting substrate and an overlying very thin PVK:TNF layer for carrier generation.

The aim of the present investigation is to study:
(a) the effect of purification on the electrophotographic characteristics of PVK.
(b) dye-sensitization of PVK with TNF,
(c) and an improvement in the performance of PVK:TNF photoreceptor plate by making double layer structure (PVK–PVK:TNF).

EXPERIMENTAL TECHNIQUES

Purification of PVK

Commercial grade PVK (Luvican M-170) as supplied by BASF (West Germany) contains as impurities 3–4% vinylcarbazole and 100–200 ppm anthracene etc. For purification, PVK is dissolved in benzene (1 g of PVK in 40 cc of benzene) and then precipitated in double volume of methanol under vigorous stirring. Since, solubility of polymer in methanol decreases with increasing molecular weight, the monomer as well as low molecular weight PVK are dissolved in methanol during the precipitation. Klöpffer[11] has estimated that after each purification cycle, the impurity and monomer content was reduced by a factor of ~10.

Sample preparation

Single layer (SL) of PVK, obtained after different purification cycles, were made by coating its toluene solution on anodized aluminium sheets. Aluminium sheets were kept in saturated toluene atmosphere to allow slow evaporation of solvent. To remove the solvent traces, the layer was dried in an air oven at 100°C

For making PVK:TNF layers, separate solutions of purified PVK obtained after 12 cycles of purification and TNF in tetrahydrofuran (THF) were mixed to form 1:1 PVK monomer to TNF molar ratio solution. This solution was coated on the anodized aluminium sheets and dried in a THF atmosphere. The THF traces were removed from the layer by heating the plate at 50°C. Thickness of PVK:TNF layer was kept ~10μm.

The DL was made by dip-coating of PVK:TNF on the SL. It results in a thin layer (~1 μm) of PVK:TNF over the thicker layer of PVK (~10 μm). The plate, thus prepared, was heated at 50°C to remove residual solvent.

Measurement techniques

The details of the experimental arrangement for corona discharge, growth and decay of surface potential of the photoreceptor have been described elsewhere[12]. The photoreceptor layer was placed below the corona wires for charging and then moved below the transparent vibrating probe for the measurement of decay rate of surface potential in dark as well as in light. A 100 watts tungsten incandescent lamp was used for photodischarging the layers. The intensity and wavelength of the light could be controlled by introducing Kodak neutral density or narrow band pass filters respectively. The light intensity in all the cases has been determined by a standard 868 Mullard photoelectric tube.

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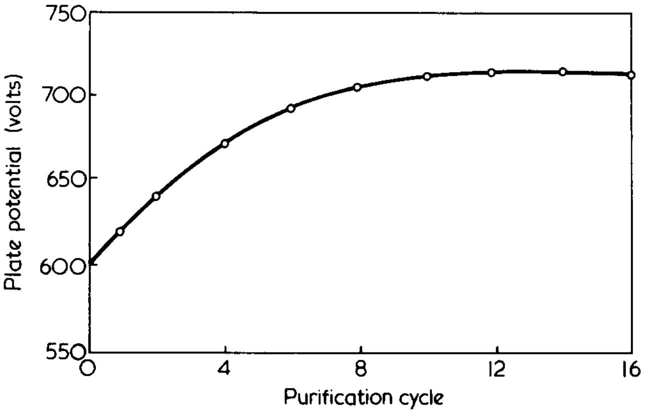

Figure 1 Plate potential versus purification cycle for PVK

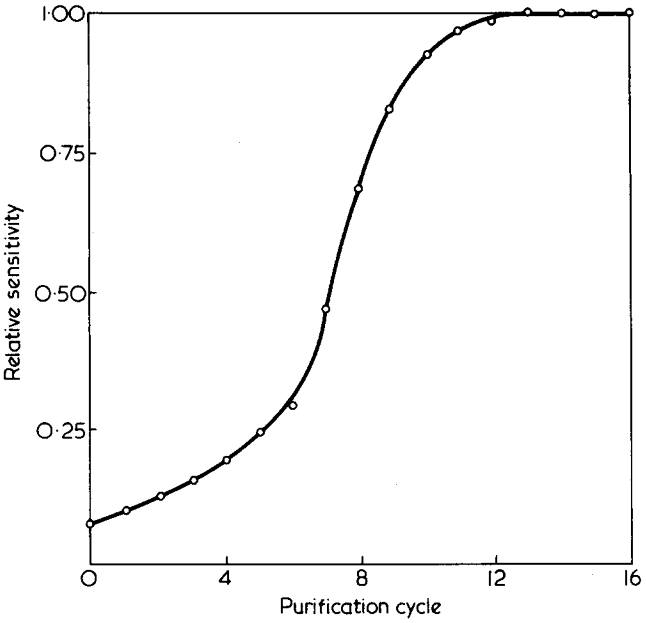

Figure 2 Relative sensitivity versus purification cycle for PVK photoreceptor at 400 nm

RESULTS AND DISCUSSION

Charging mode consideration

The results on the effect of charging on surface potential of PVK and PVK:TNF with different TNF concentrations have been given by Schaffert[9]. The unsensitized PVK possesses good charge acceptance in the positive mode, whereas in the PVK:TNF system (1:1 molar ratio), the charge acceptance in the negative mode is significantly high.

In the case of DL, the positive charging mode has shown the most satisfactory dark and light decay characteristics. The light absorbed in the PVK:TNF layer generates electron-hole pairs, of which, electrons neutralize the surface charge and holes are emitted into the PVK layer. The mobility of holes in PVK is rather high (10^{-6}cm^2 sec^{-1} V^{-1})[13] and the concentration of hole trapping centres is small ($\sim 10^{13}$cm^{-3})[14]. Hence holes are swept away from the PVK layer very fast, suffering only negligible trapping. In the case of negative charging mode, the electrons transported through the PVK layer are severely trapped[15] causing residual potential and, hence, drastically decreasing the contrast potential during repeated charging and development cycle.

So, for pure PVK and DL, positive charging mode, while for PVK:TNF, negative charging mode was chosen. Other charging parameters are:

corona voltage	6 kv	ac
grid voltage	0–1.5kv	dc
time of charging	10 sec	

Effect of purification

Effect of purification of PVK on electrophotographic characteristics is measured in terms of charge acceptance, relative sensitivity and contrast potential. Relative sensitivity is measured from the photoinduced decay data for 400 nm light.

The contrast potential, which determines the limit of the image development and the quality of the final print, is measured from the light decay data for different exposures and finally an optimum purification stage is found for the best electrophotographic results.

Figure 1, shows the effect of purification on plate potential. In the beginning, plate potential increases with purification but after 10 cycles it becomes constant and further purification does not improve it.

Figure 2 shows relative sensitivity versus purification cycle using light of wavelength 400 nm. It is observed that there is a significant increase in the sensitivity with each purification cycle and after 12 cycles it becomes constant (*Figure 3*).

The results shown in *Figure 3* are in good agreement with the results of *Figure 4* where contrast potential is plotted for different exposures. The inset of *Figure 3* gives contrast potential versus purification cycle which shows that contrast potential increases with purification up to 12 cycles and then becomes constant.

Hence, PVK obtained after 12 cycles of purification has been used in making SL, PVK:TNF and DL photoreceptors.

Effect of charge transfer complex with TNF

The section describes the improvement in the various electrophotographic properties such as charge acceptance, contrast

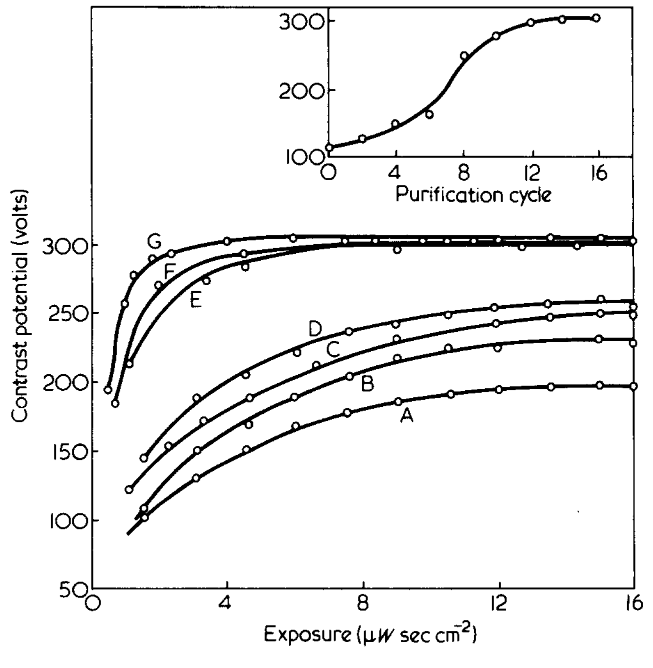

Figure 3 Contrast potential versus exposure for PVK under different cycles of purification. A corresponds to impure PVK while B, C, D, E, F and G correspond to PVK obtained after 2, 4, 6, 8, 10 and 12 cycles of purification respectively. Inset: Contrast potential versus purification cycle of PVK

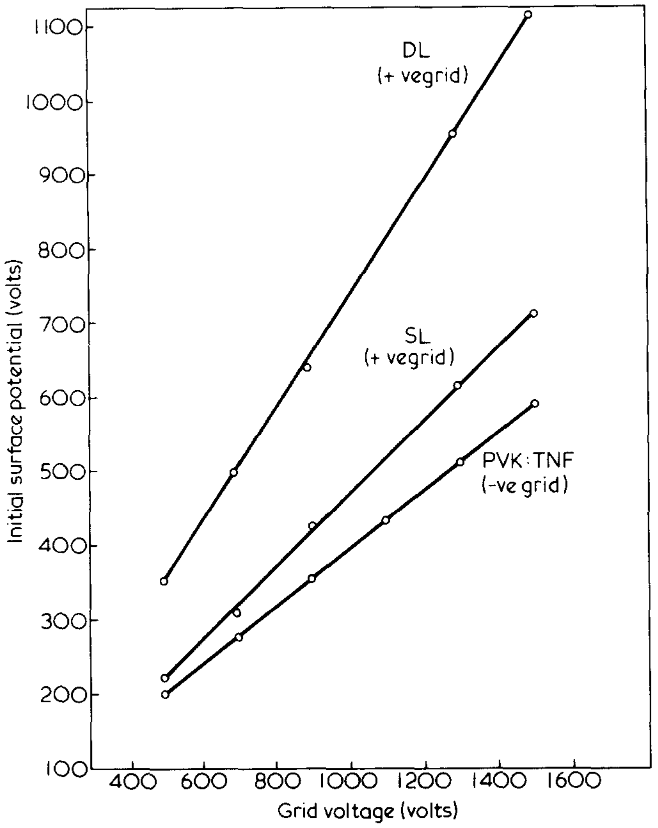

Figure 4 Initial surface potential versus grid voltage for PVK (SL), PVK:TNF and PVK–PVK:TNF (DL) photoreceptors

potential, sensitivity and quantum efficiency of PVK:TNF and PVK–PVK:TNF (DL) photoreceptor[5].

Charge acceptance and dark decay. The initial surface potential accepted by the SL, PVK:TNF and DL under different grid potentials are shown in *Figure 4*. It is evident from the curves that DL accepts more charge as compared to SL and PVK:TNF layers.

The dark decay characteristics of the surface potential (shown in *Figure 5*) show very fast decay (half decay time for PVK:TNF layers ~70 sec), while in the case of SL and DL photoreceptors the dark decay is quite slow. The fast decay in the case of PVK:TNF can be explained on the basis of increased dark conductivity of PVK upon doping with TNF making it undesirable for electrophotographic applications.

Contrast potential. Figure 6 depicts the dependence of contrast potential on exposure for SL, PVK:TNF and DL photoreceptors. In the case of SL, the contrast potential increases continuously with exposure, whereas an optimum exposure of 1 $\mu W/sec/cm^{-2}$ and 0.4 $\mu W\ sec/cm^{-2}$ is found for PVK:TNF and DL photoreceptors, respectively. The better performance of DL photoreceptors is exhibited in its higher contrast potential ~600v for an initial potential of V_0 ~750 v, while for SL and PVK:TNF, the contrast potentials have been observed much lower (*Figure 6*).

Spectral sensitivity. The wavelength dependence of photo-induced discharge characteristics provides the basic data for determining the spectral sensitivity of the electrophotographic photoreceptors. The decay rate of surface potential depends primarily upon quantum efficiency for exciting charge carriers (electrons, holes or both) to a state of conduction, and upon the effective mobility of these carriers. The number of carriers released for conduction will also depend upon the amount of incident light within the layer and the energy per photon as determined by the wavelength or range of wavelengths of the incident radiation.

The relative spectral sensitivity of SL, PVK:TNF and DL photoreceptors are shown in *Figure 7*. The enhancement of sensitivity for DL is quite significant. The shift of the spectral sensitivity maximum towards the visible region in the DL is also a desirable aspect for electrophotographic applications as white light illumination could be used for the exposure.

Quantum efficiency. The effective quantum efficiency η_λ, for neutralization of surface charge due to incident photons is given by[16]

$$\eta_\lambda = \frac{\Delta\sigma}{N_\lambda}$$

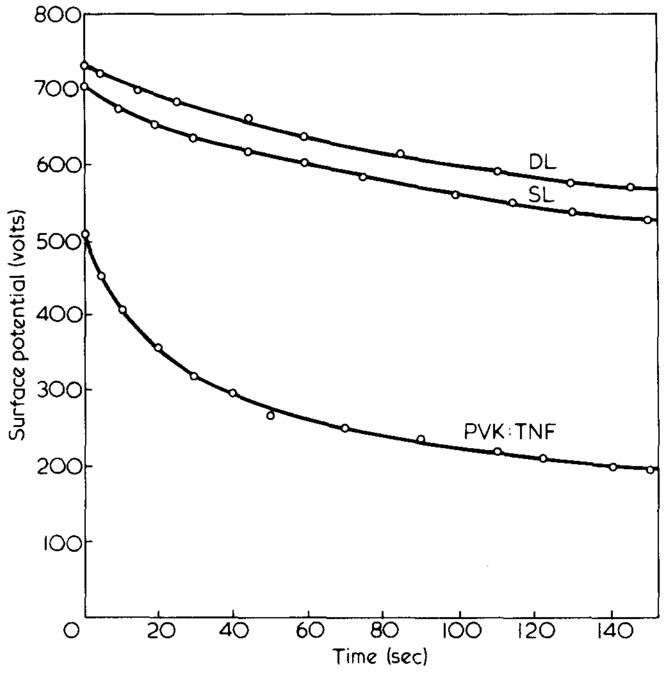

Figure 5 Dark decay of surface potential for PVK (SL), PVK:TNF and PVK–PVK:TNF (DL) photoreceptors

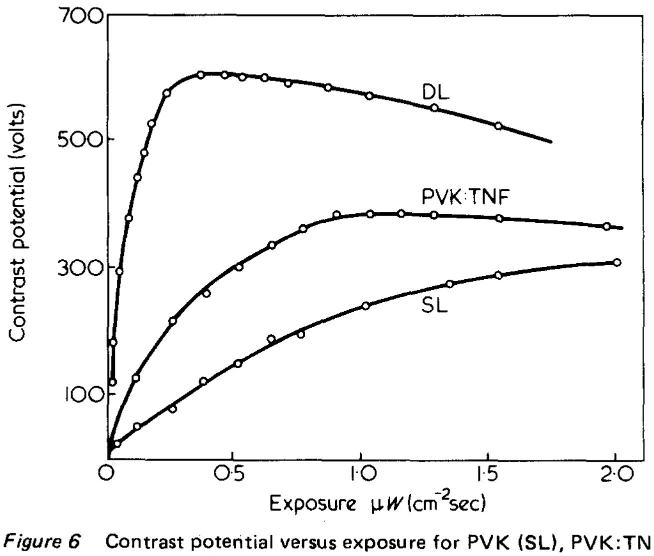

Figure 6 Contrast potential versus exposure for PVK (SL), PVK:TNF and PVK–PVK:TNF (DL) photoreceptors

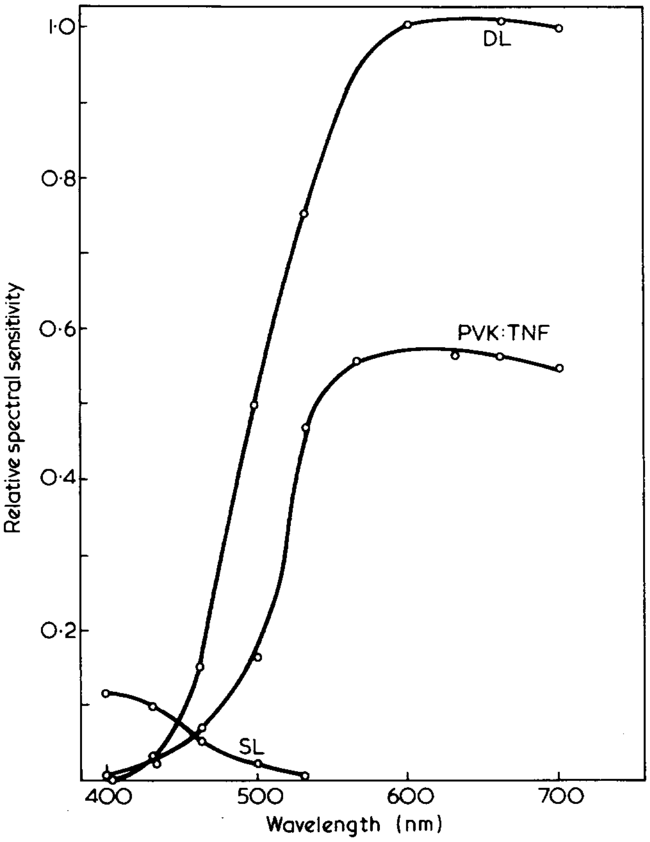

Figure 7 Relative spectral sensitivity versus wavelength for PVK (SL), PVK:TNF and PVK–PVK:TNF (DL) photoreceptors

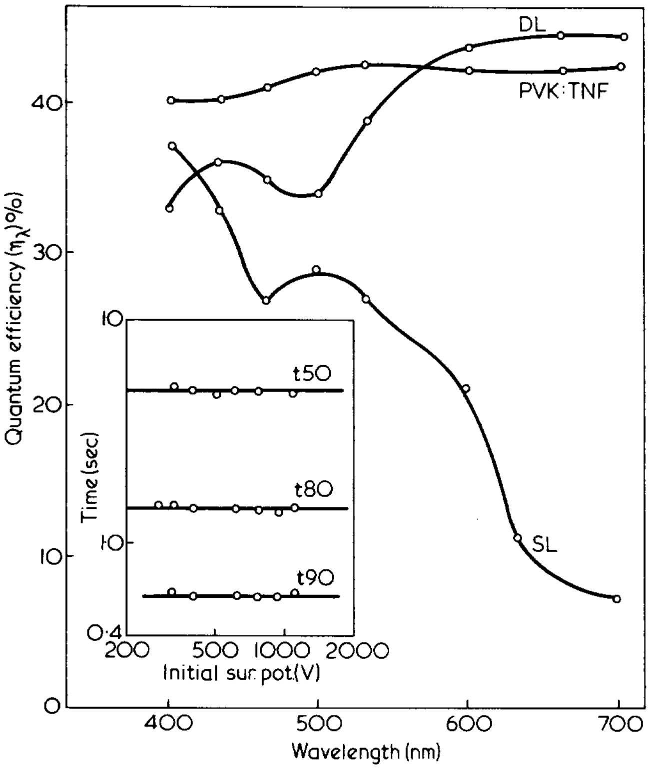

Figure 8 Quantum efficiency versus wavelength for PVK (SL), PVK:TNF and PVK–PVK:TNF (DL) Photoreceptors. Inset: Discharge rate versus initial potential for DL with ~1 μW cm^{-2} white illumination. t_{90}, t_{80} and t_{50} refer to the exposure times required to reduce the surface potential to 90%, 80% and 50% of the initial potential.

where, $\Delta\sigma$ is the reduction of surface charge density in electron units per cm^2, when the surface is irradiated with light of wavelength λ for a given time and N_λ is the number of photons per sq. cm. incident upon the surface during the same period. In terms of the surface voltage, η_λ can be written as,

$$\eta_\lambda = \frac{k\Delta V\eta}{LI_0} \times 8.85 \times 10^{-6}\,(\%)$$

where k, the dielectric constant; ΔV, the reduction in the surface voltage in volts; n, electron-volts per photon; L, the thickness of the photoreceptor in cm and I_0, the light intensity in μw cm^{-2}. If R_λ is the reflectivity of the surface, the intensity I_0 in the above expression can be replaced by $I = I_0\,(1 - R_\lambda)$ for accurate results.

Figure 8 shows that the quantum efficiency in the visible region is considerably more in PVK:TNF and DL photoreceptors as compared to that in SL photoreceptors. The DL photoreceptors show a peak at lower wavelength due to the underlying layer of PVK, whereas in the case of PVK:TNF, the quantum efficiency curve is almost flat. The inset of *Figure 8* shows the dependence of discharge rate on the initial potential. The curves are almost parallel to the abscissa, showing that the discharge rate is independent of the initial potential. The quantum efficiency for the hole generation is, therefore, proportional to the average electric field[17,18].

SUMMARY AND CONCLUSIONS

The work presented in the paper is essentially concerned with the evaluation of electrophotographic characteristics such as contrast potential, spectral sensitivity, quantum efficiency from the photoinduced discharge of PVK (SL), PVK:TNF and PVK–PVK:TNF (DL) photoreceptors. Effect of purification of PVK on these characteristics is also studied. The results are summarized as below:

(i) acceptance potential, contrast potential, photosensitivity of PVK are greatly increased on purification as shown in *Figures 1, 2* and *3*,

(ii) sensitizing with TNF improves the spectral response (*Figure 7*) but acceptance potential and contrast potential (*Figure 4* and *6* respectively) have decreased.

(iii) double layer structure (PVK–PVK:TNF) gives best electrophotographic performance as compared to PVK and PVK: TNF photoreceptors, as in DL acceptance potential, contrast potential and spectral sensitivity are observed to be higher.

These results lead to the conclusion that DL is well suited for eletrophotographic applications as it possesses contrast potential (>400v) and a broad spectral sensitivity peak in the visible region.

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