

A New High-sensitivity Organic Photoconductor for Electrophotography*

Abstract: A new organic photoconductor has been developed, consisting essentially of a 1:1 molar ratio of one molecule of 2, 4, 7-trinitro-9-fluorenone (TNF) to one monomer unit of poly-N-vinylcarbazole (PVCz). This photoconductor (1:1 TPC) is nearly pan-chromatic in the visible range of the spectrum and has a white-light sensitivity approximately equal to that of amorphous selenium when used for electrostatic imaging. The photosensitivity, which is due mainly to the TNF-PVCz complex, is greater for negative corona charging than for positive charging. Charge acceptance of the 1:1 TPC is high, ≈ 1200 volts for a $13\mu\text{m}$ film, indicating good dielectric strength. Dark decay of the charge is affected by substrate materials and substrate surface conditions. In general dark decay is slower for negative charging than for positive charging. Quantum efficiency (Q. E.) is nominally about 0.15 in the range of 400 to 500 nm but decreases somewhat for shorter and longer wavelengths. The Q.E. increases rather markedly with field strength, but decreases somewhat at high light intensities. Field-controlled photogeneration of carriers is indicated, and thermal measurements show a field-dependent activation energy in the range of 0.06 to 0.20 eV. The absence of residual potentials in light decay curves and the lack of a thickness effect in photodischarge currents indicate that no deep traps are present in the 1:1 TPC layers.

Introduction

An organic-polymeric photoconductor having a photosensitivity much greater than any previously reported for organic materials has been developed at IBM for use in electrophotographic processes. This unique electrophotosensitive material was originally formulated by M. D. Shattuck and U. Vahtra [1] of IBM during experiments on the sensitizing of polyvinylcarbazole when they succeeded in combining trinitrofluorenone with the polymer in concentrations many times greater than the amounts usually considered maximum for photosensitization.

The photoconductor in its final form consists essentially of a 1:1 ratio of one monomer unit of poly-N-vinylcarbazole (PVCz) to one molecule of 2, 4, 7-trinitro-9-fluorenone (TNF). The TNF (electron acceptor) forms a charge transfer complex with the PVCz (donor) which is essentially amorphous. This material absorbs light throughout the visible range of the spectrum. Photoconducting films therefore, have a dark brown, nearly black appearance.

Such films provide reusable photoconductive insulating layers. They have high charge acceptance for corona charging and low dark decay rates and are therefore quite suitable for use in the photoelectric formation of

electrostatic images. The films are also tough and durable and these properties, together with negligible fatigue effects, make them suitable for applications requiring a reusable photosensitive medium such as in photocopying and duplicating.

Historical background

Hoegl, Sus, and Neugebauer [2] apparently were the first to report on the photoconductivity of polyvinylcarbazole and to propose its use in electrophotography. They also found that the photosensitivity of this polymer could be increased by small additions of dyestuff compounds and various other organic compounds such as carboxylic, sulphonic, and phosphonic acids, acid anhydrides, nitrophenols, quinones, aldehydes, and ketones. The amounts of sensitizers and additives incorporated into the PVCz were generally in the range of about 0.01 to 5% by weight but it was mentioned that quantities up to 20% by weight could be used. While these amounts usually resulted in increases in photosensitivity over that of unsensitized PVCz, the level of sensitivity apparently was still considerably below that of photoconductive materials used in commercial electrophotographic machines.

Hoegl and Neugebauer [3] mention 2, 4, 7-trinitrofluorenone as one of a long list of "activator" compounds that form charge transfer (CT) complexes with polymers

* This paper is a critical analysis and condensation of work done by the inventors of this new organic photoconductor, M. D. Shattuck and U. Vahtra, and by a number of other investigators, as noted in the acknowledgments at the end of this paper.

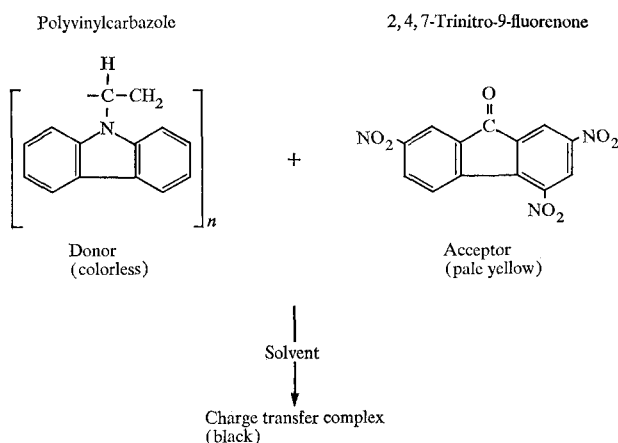


Figure 1 Formation of the charge transfer complex with polyvinylcarbazole and 2,4,7-trinitro-9-fluorenone.

derived from polynuclear aromatic vinyl compounds. They found that additions of such activator materials in amounts ranging from 0.0001 to 0.1 moles (preferably from about 0.001 to 0.05 moles) per mole of the photoconductive substance increased the light sensitivity, particularly within the ultraviolet range of the spectrum. Inclusion of very small amounts of dyestuff sensitizers in addition to the activator substances extended light sensitivity into the visible range. Further investigations reported by Hoegl [4] were also limited to low concentrations of the sensitizing materials.

Hayashi, Kuroda and Inami [5] investigated PVCz with dye sensitizers of 0.05% by weight, and Lewis acid-type sensitizers of 1 to 10% by weight, as well as combinations of the two types of sensitizers. They concluded that the systems containing quinones were the most useful for electrophotography. The systems containing strong acids were found to be impracticable because of their rapid dark decays and persistent memory effects.

Lardon, Lell-Doller, and Weigl [6] investigated the effects of several electron acceptor dopants, including TNF, on the photoconductivity of PVCz. Concentrations of acceptor materials were again quite small—up to about 6.3 mole% (9.3% by weight). They concluded that the sensitivity of PVCz was extended into the CT bands of the complexes, but the intrinsic ultraviolet response of the PVCz was not appreciably enhanced by complexing.

Recently Gasner and Wagner [7] reported on experiments with PVCz doped with 0.8 mole % of π -electron acceptors, including TNF. Their results indicate that neither the electron affinity of the dopant nor the optical absorption of the CT complex can be used to predict photoresponse.

The reasons for which previous investigators limited the additions of sensitizing materials to such small concentrations can only be surmised. These concentration levels are in the range usually associated with photographic

sensitization and are probably within optimizing limits when dyestuffs are used. However, in the case of organic electron acceptor materials the formation of charge transfer complexes provides a different type of sensitizing mechanism. Such materials can no longer be regarded primarily as dopants but rather should be looked upon as major constituents of the photoconductive composition. It is true, however, that many of the acceptor and donor materials, mentioned in previous patents and publications as sensitizers for PVCz, have an adverse effect on sensitivity at high concentration levels, and may also result in increased dark decay and poor charge acceptance. Experiments with higher concentrations of such materials may have discouraged further exploration in this direction. Sharp [8] found that additions of picryl chloride to single crystals of N-isopropylcarbazole (1% and 1:1 mole %), had little or no effect on the photoconductivity of the parent crystal.

Composition and structure

The TNF-PVCz complex is formed by direct reaction of the two materials in a suitable solvent, e.g., tetrahydrofuran (THF) (see Fig. 1). The equilibrium constant for the formation of this complex in THF was found to be 1.31 mole^{-1} at room temperature.

X-ray analysis of the 1:1 CT complex shows an amorphous polymer-like form with no free TNF. The exact structure of TNF-PVCz material is not known. A reasonable postulation is that TNF and carbazole rings overlap with TNF molecules sandwiched between carbazole units, providing alternate charge transfer linkages in the polymer-like chain.

• Preparation of coatings

Laboratory samples of the TNF-PVCz photoconductor can be prepared by dissolving the two constituents in tetrahydrofuran (THF) [9]. From the standpoint of producing films free of surface crystals, THF was found to be the best solvent. Chlorobenzene gave good results when the films were applied hot, and 1, 2-dichloroethane was usable but gave somewhat inferior results. The usual procedure is to make up a stock solution of PVCz in THF. The TNF is then added in the amount necessary to provide the desired molar ratio. This is followed by rolling to insure complete dissolution of the TNF. Photoconductive films can then be obtained by coating the solution onto a suitable substrate, followed by heat curing to remove the solvent.

Films prepared in the above manner consist primarily of the TNF-PVCz complex. When films are prepared for continuous machine usage, three additional ingredients are usually added: (1) an adhesive to insure good bonding to the substrate, (2) a plasticizer to improve flexibility, and (3) a film former to insure smooth, uniform films.

In some cases the adhesive and plasticizer can be one material. However, unless otherwise stated, all samples used in the experiments described in this paper consist of the unmodified 1:1 TPC, prepared from Luvican M-170† (PVCz) and purified TNF.

• *TNF concentrations*

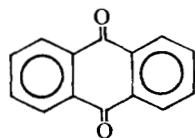
Selection of the 1:1 molar ratio of TNF to vinylcarbazole (1:1 TPC) as an optimum composition is based on experimental tests using electrostatic imaging techniques for comparative measurements. Usually, for relative measurements of photosensitivity, sample films of essentially equal thickness are each charged electrically to the same surface potential with a corona charging device. Charge decay is then monitored with a recording electrometer during illumination of a film with a constant-intensity light source. The reciprocal of the exposure time required to reduce the surface potential to one-half its initial value is taken as a relative measure of sensitivity for practical tests.

The above technique was used to obtain the data shown in Fig. 2, which is a plot of relative sensitivity vs concentration of TNF in PVCz. In this experiment the light source was a tungsten lamp. It can be seen from Fig. 2 that the sensitivity reaches a maximum value at about a 1:1 molar ratio of the two constituents for negative charging and at about a 0.8:1 molar ratio for positive charging.

Concentrations of TNF beyond the 1:1 molar ratio do not produce any improvement in sensitivity. Films with TNF concentrations greater than the 1:1 ratio can be obtained without surface crystallization, but such films are more difficult to prepare.

• *Other charge transfer sensitizers*

Experiments show that other acceptor molecules that form CT complexes with PVCz can be used to sensitize PVCz at high concentration levels. However, none has been found to be as good as TNF. Although no acceptor molecules were found that produce a sensitized PVCz photoconductor equal or superior to the TNF/PVCz complex, a few were identified that show promise as potentially good sensitizers for PVCz. Among these were the substituted anthraquinones, having the structure



particularly the chlorine-hydroxy-, and nitro-substituted anthraquinones. Experimental PVCz samples selected from this group exhibited photoresponses in which con-

† Badische Anilin Soda-Fabrik AG.

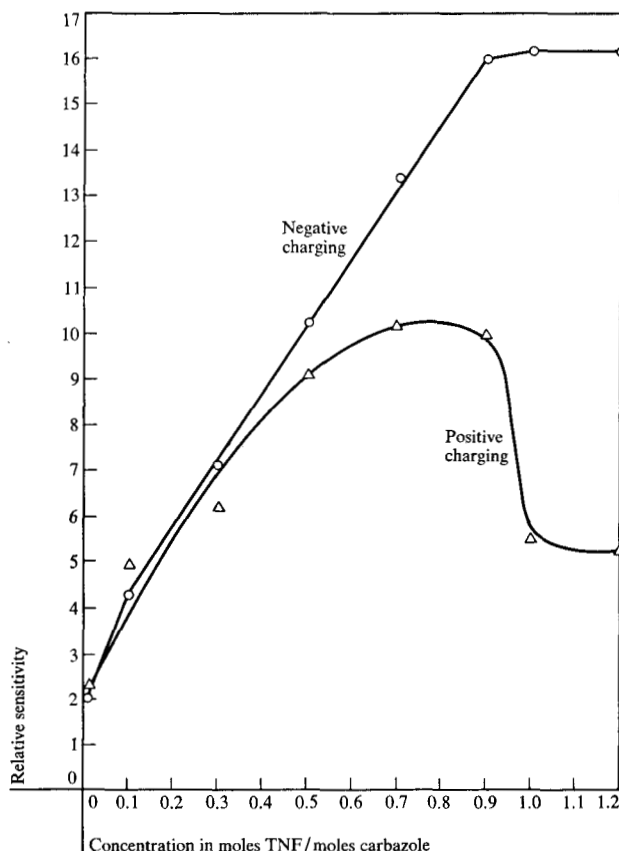
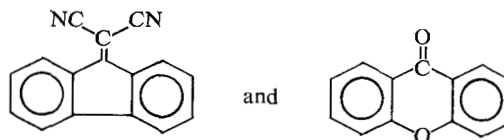


Figure 2 Photosensitivity as a function of TNF concentration in PVCz.

ductivity ranged from about 0.1 to 0.2 relative to the 1:1 TPC under illumination with a tungsten lamp, and from about 0.15 to 0.60 when exposed at 450 nm. Molar concentrations of these sensitizers at optimum photosensitivity ranged from 0.1 to 0.5.

Other groups which showed good photosensitization of PVCz were the nitrated fluorenone-like structures, e.g.,



PVCz samples sensitized with selected compounds from these groups exhibited relative sensitivities ranging from 0.05 to 0.6 for tungsten light and from about 0.1 to 0.5 for monochromatic exposure at 450 nm. Molar concentrations for optimum sensitization ranged from 0.1 to 0.7.

In general the substituted benzenes exhibited rather poor photosensitization of PVCz compared to TNF. An exception was 1, 3, 5-trinitrobenzene, which showed rela-

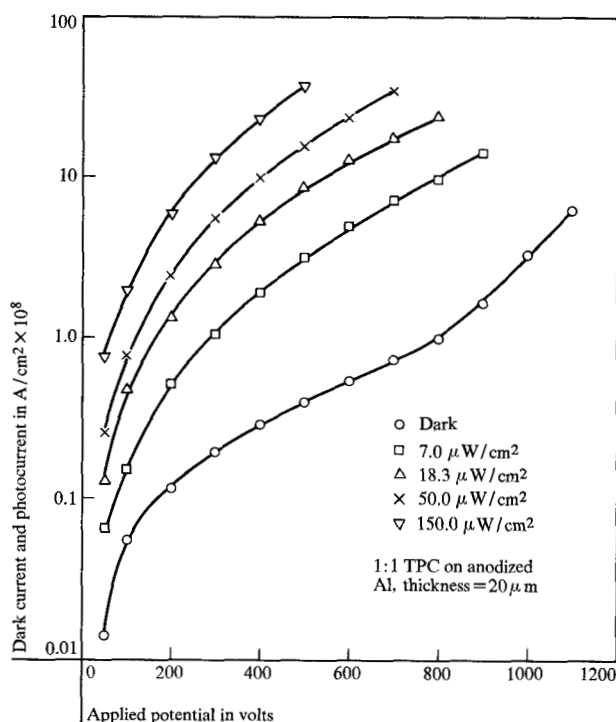


Figure 3 Current-voltage curves for a typical 1:1 TPC sample. Data were obtained by means of screen-controlled corona charging.

tive sensitivities of 0.14 and 0.3 for tungsten and 450 nm, respectively, with an optimum molar concentration of 0.8.

The compounds available for this investigation were not suitable for systematic comparisons of group substitutions. There were some indications that structural planarity of the sensitizer molecule may be an important parameter.

Electrical and optical properties of 1:1 TPC films

• Photoconductivity

Dark currents and photocurrents for various 1:1 TPC samples were measured by means of a screen-controlled corona charging technique similar to that used by Lardon, Lell-Doller and Weigl [6]. The light source used was a 110 W incandescent projector lamp. Current-voltage curves for a typical film sample are shown in Fig. 3. The photocurrents (J_p) plotted in Fig. 3 are corrected for dark current (J_d) i.e., $J_p = J_t - J_d$, where J_t is the total current during exposure to light. It is apparent that there is no simple mathematical relationship between current and voltage. At the higher voltages the photocurrent approximates a power-law relationship with applied voltage, $J_p \propto V^n$, with $n \approx 2.3$. The dark current exhibits a steep nonlinear rise with voltage at the lower voltages, followed

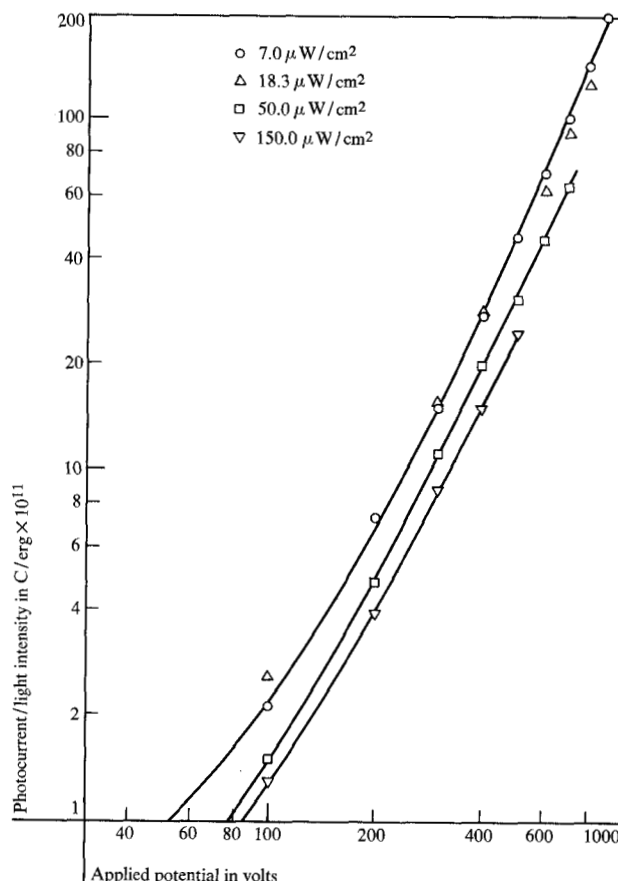
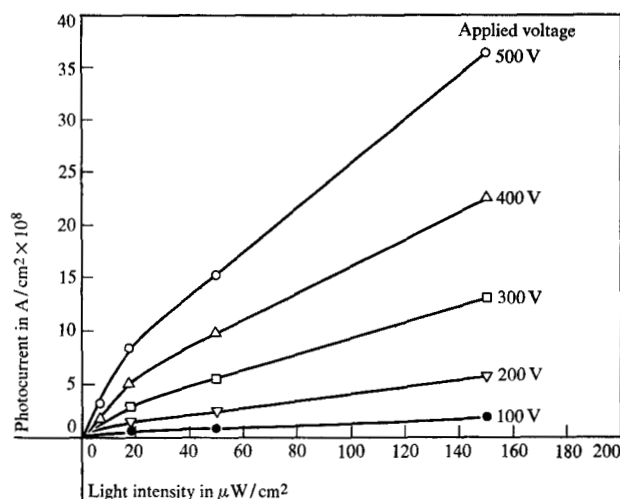


Figure 4 Ratio of photocurrent to light intensity as a function of applied voltage for a 20 μm layer of 1:1 TPC.

Figure 5 Photocurrent vs light intensity for a 1:1 TPC sample.



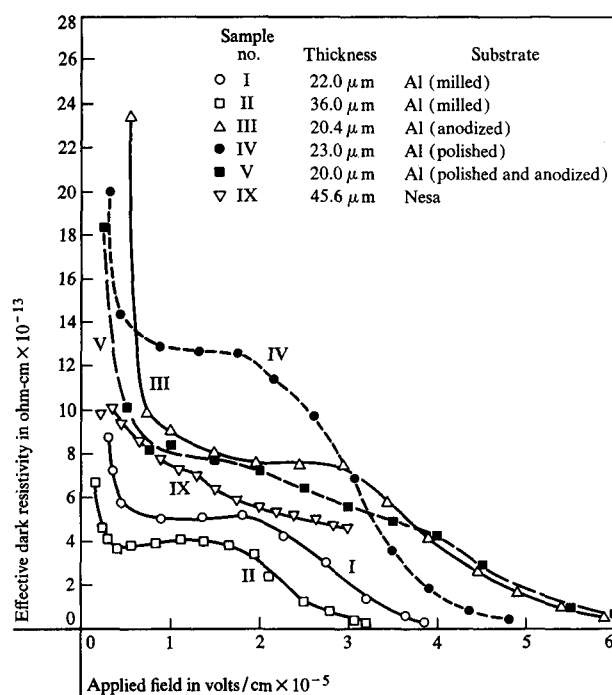


Figure 6 Dark resistivity vs applied field for several samples of 1:1 TPC coated on various substrates.

by a slower, nearly exponential rise in the intermediate voltage range, and a relatively sharp rise in the high voltage range.

Figure 4 shows the ratio of photocurrent to light intensity as a function of applied voltage. The photoconductive gain is a rather steep function of the voltage across the layer. A 200-fold increase is evident in the range of 50 to 900 V. The gain is somewhat greater at low intensities than for the higher intensities. There appears to be a leveling off at lower light intensities. This is apparent in Fig. 4, where the curves for light intensities of 7.0 and 18.3 $\mu\text{W}/\text{cm}^2$ nearly coincide.

The increase of photocurrent with light intensity is shown in Fig. 5. The data available for plotting the curves in Fig. 5 are too sparse for precise evaluations. However, the current increase is roughly proportional to the 0.75 power of light intensity for the voltage range indicated here.

• Dark resistivity

It is known that the effective dark resistivity of photo-sensitive layers used in electrophotography is not simply a bulk property, but depends to a large extent on the interaction between the conductive substrate and the layer. This is indicated in Fig. 6, where differences in dark resistivity among the various samples are apparent.

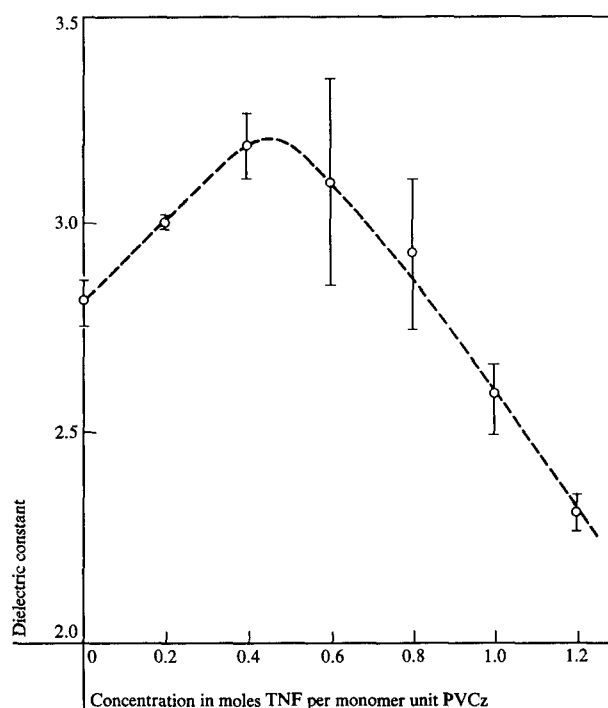


Figure 7 Dielectric constant as a function of TNF concentration for TNF/PVCz photoconductors.

The effective dark resistivity at high field strengths is important in electrostatic imaging. A higher dark resistivity in the high-field region provides higher charge acceptance and slower dark decay of surface charge. The samples coated on anodized aluminum appear to be best for this purpose.

The effective dark resistivity decreases rather markedly as the electric field across the sample increases. There is approximately an order of magnitude decrease within the ranges shown in Fig. 6. Most of the curves exhibit a plateau in the intermediate field strength region where the resistivity is nearly constant. The data used in plotting the curves of Fig. 6 were obtained from dark current-voltage curves similar to the one shown in Fig. 3. All experiments were conducted at room temperature with negative potentials applied to the screen and corona wires.

• Dielectric constant

The dielectric constant of the 1:1 TPC was found to be 2.6 ± 0.1 when measured with a capacitance bridge operating at 200 Hz. The dielectric constant varies with the amount of TNF added to PVCz. As the concentration increases the dielectric constant first increases and then decreases (see Fig. 7). The above value is somewhat lower than the value of 3.4 calculated by the author from corona charging data.

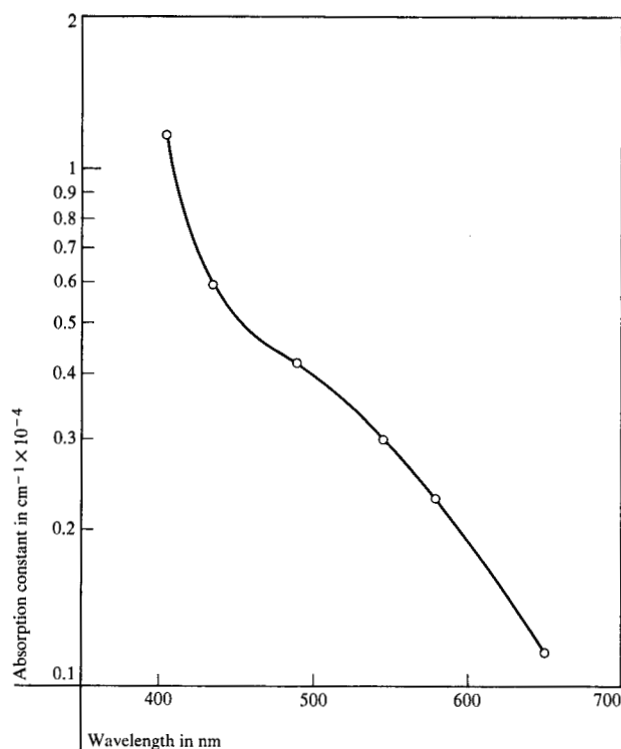
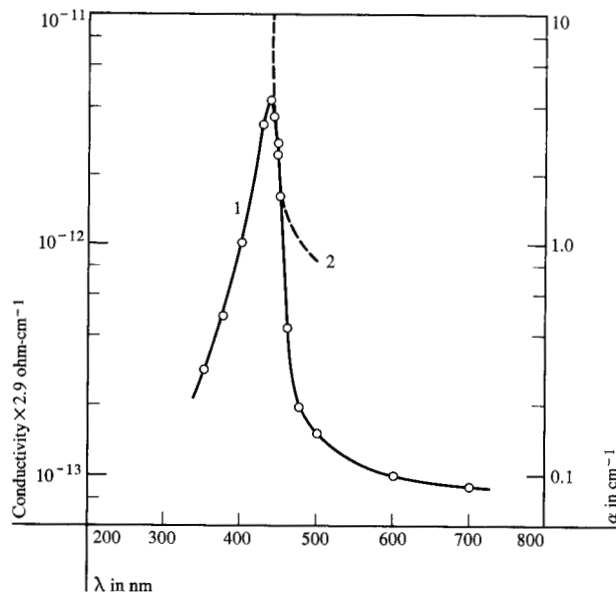


Figure 8 Absorption spectrum of the 1:1 TPC.

Figure 9 (1) Photoresponse curve for a TNF single crystal. The field across the crystal is 4×10^3 V/cm (left scale). (2) The optical absorption coefficient (right scale).



It should be pointed out also that the value of 2.8 ± 0.06 for the dielectric constant of PVCz, as shown in Fig. 7, is considerably less than the value of 3.75 ± 0.4 at 10 Hz given by Regensburger [10]. The differences here need to be clarified by further measurements.

• Absorption spectra

The 1:1 TPC shows relatively good light absorption throughout the visible range of the spectrum with strong absorption occurring at wavelengths of about 400 nm and less (see Fig. 8). The data in Fig. 8 indicate that light penetration depths for 90% absorption are about 2.0 μm at 400 nm, 6.0 μm at 500 nm, 11.8 μm at 600 nm, and 20.0 μm at 650 nm. Thus, films less than 20 μm thick will not absorb all of the penetrating light at the longer wavelengths during one trip through the film. However, back reflection from the substrate, plus some internal reflection, will probably increase the total absorption in films used for electrostatic imaging.

The greater amount of absorption in the visible part of the spectrum is due primarily to the TNF/PVCz complex, while the absorption in the near-ultraviolet can be attributed mainly to the polymer and the TNF sensitizer. Lardon et al. [6] measured the absorption spectra of the complex and the separate components in dilute benzene solutions. They place the absorption peak for the complex at 502.5 nm, while their data for absorption of the two individual components indicate strong absorption peaks in the short-wavelength region with long-wavelength cutoff for PVCz and TNF at about 370 nm and 450 nm, respectively.

The cutoff for TNF agrees well with data on single crystals of this compound. The crystals were found to be photoconducting with a sharp absorption edge near 450 nm, as shown in Fig. 9. Optical absorption data on the same crystal showed a cutoff at the same wavelength, indicating intrinsic photoconductivity with a band gap of 2.8 eV.

• Reflectance spectra

Reflectance as a function of wavelength is shown in Fig. 10 for three 1:1 TPC samples of different thicknesses coated on aluminized substrates. Surface reflection is less than 10 percent for the greater portion of the visible spectrum with a rather sharp increase in the long-wavelength region. The greater reflectance for the thinner films in the 600 to 700 nm range is probably a substrate reflection effect. Since absorption in this range is small, less of the back-reflected beam will be absorbed internally for the thinner films. In the 400 to 600 nm range essentially all of the light penetrating into the film is absorbed.

• Other physical properties

Prepared films of the 1:1 TPC are normally rather rigid and inelastic, with a critical surface tension estimated to be about 40 dynes/cm. Flexibility can be improved by adding small amounts of plasticizers and modifiers to the formula. Young's modulus for the modified form is about 1.4×10^{11} dynes/cm². Density of the 1:1 composition was found to be 1.43 gm/cm³.

Thermal stability of the 1:1 TPC material is very good. In accelerated aging tests film samples were not adversely affected when heated at 70°C for periods up to six weeks. However, heating at 130°C for four hours or more produced gross crystallization of the film. Thermal analysis produced endotherms at 148 and 168°C. The first of these was found to be associated with softening of the material and dissociation of the complex resulting in free crystalline TNF. The second endotherm (168°C) was associated with melting of the residual mixture. An exotherm observed at 365°C marked the onset of complete thermal degradation of the material.

Electrophotographic characteristics

The behavior of 1:1 TPC in electrostatic imaging procedures can vary over a relatively wide range depending on such things as the method of preparation, the degree of purity of constituents, additives, the nature of the substrate surface upon which the material is coated and the thickness of photoconductor layers. Unless otherwise stated, all experimental data given below were obtained at room temperature using 1:1 TPC prepared from Luvican M-170 and purified TNF.

• Charge acceptance

It is known that the amount of charge (surface charge density) that can be applied to and retained on a photoconductive insulating layer in the dark is an important factor in electrophotographic processes utilizing electrostatic imaging techniques.

Generally it is not difficult to charge relatively thin layers of the 1:1 TPC to relatively high voltages. For example, a film 13 μm thick can easily be charged to 1200 V with a suitable corona unit. This produces a surface charge of $0.225 \mu\text{C}/\text{cm}^2$, which is much more than is necessary for the electrostatic contrast needed to develop dense images. Surface potentials in the range of 600 to 800 V are usually sufficient.

It has been shown in a previous publication [11] that charge acceptance is not an independent property of the electrophotographic plate, but is dependent also upon corona charging conditions. When the cutoff plate potential for the corona unit is greater than the maximum acceptance potential of the charged layer, the leakage current through the layer will eventually become equal to the corona current as charging proceeds. Further increase in the applied corona voltage and consequent corona current will then increase the acceptance potential of the layer until the true maximum is reached. At this point, which is probably near dielectric breakdown, further increase in corona voltage will not increase charge acceptance of the layer. Maximum charge acceptances obtained in this manner for several samples of the 1:1 TPC are shown in Fig. 11. The samples are all of the same formu-

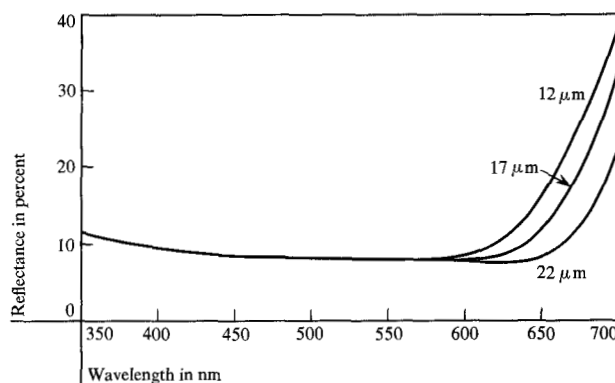
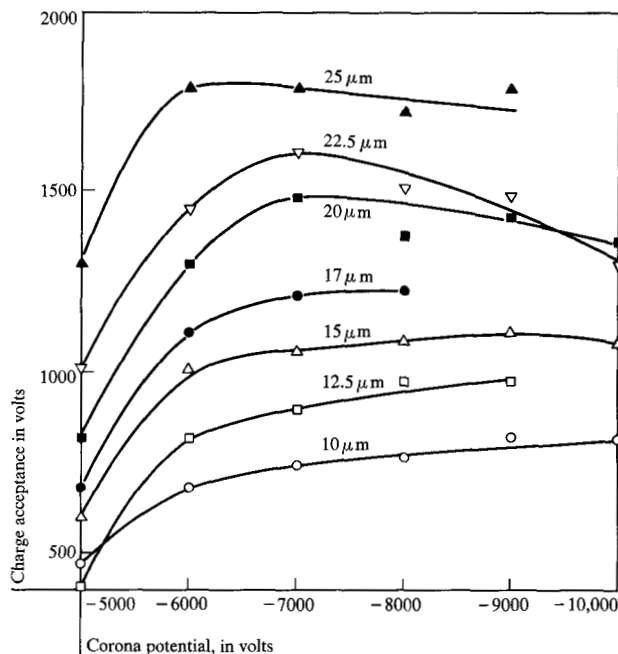


Figure 10 Reflectance spectra of several 1:1 TPC samples.

Figure 11 Negative charge acceptance vs corona voltage for sample films of 1:1 TPC with different thicknesses. Thickness values are estimates based on wet gaps.



lation, but vary in thickness from about 10 to 25 μm . It can be seen that the maxima are reached at lower corona voltages for the thicker samples than for the thinner samples. The charge acceptance of most of the samples tends to level off after reaching a maximum value. However, several samples show a decrease from the maximum value with further increase of the corona voltage, indicating some dielectric breakdown in localized areas.

Figure 12 shows that the negative charge acceptance potential increases with sample thickness. This increase is nearly linear for the higher corona voltages, but departs considerably from linearity at lower corona voltages. Cal-

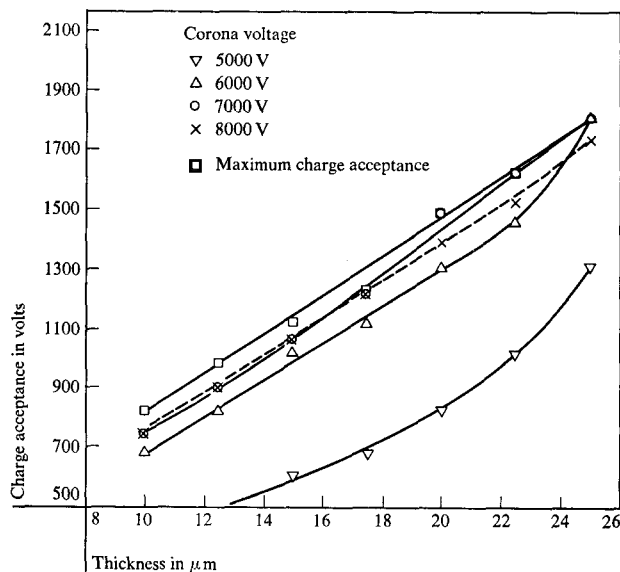
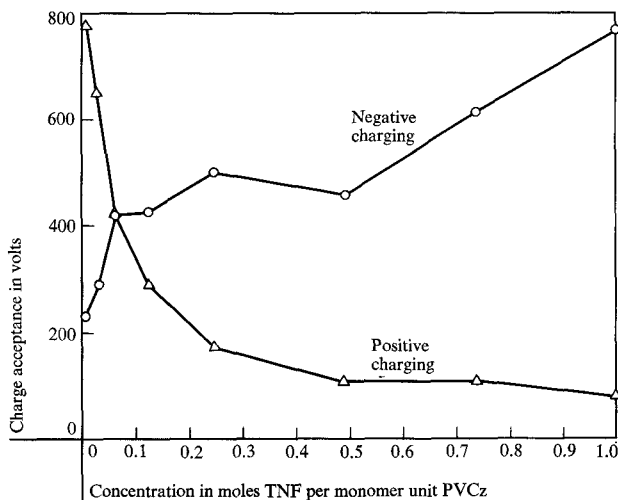


Figure 12 Negative charge acceptance as a function of thickness for the 1:1 TPC. Samples are the same as in Figure 11.

Figure 13 Charge acceptance as a function of TNF concentration for TNF/PVCz coatings on a clean aluminum substrate (not anodized).



culations, taking into account the capacitance of the 1:1 TPC layers, show that the maximum surface charge acquired by the layers is $1.71 \times 10^{-7} \text{ C/cm}^2$ for the $25 \mu\text{m}$ layer and $1.96 \times 10^{-7} \text{ C/cm}^2$ for the $10 \mu\text{m}$ layer. The corresponding field strengths are $7.16 \times 10^5 \text{ V/cm}$ and $8.2 \times 10^5 \text{ V/cm}$, respectively. These results indicate that the thinner films will sustain somewhat higher charge levels than the thicker films.

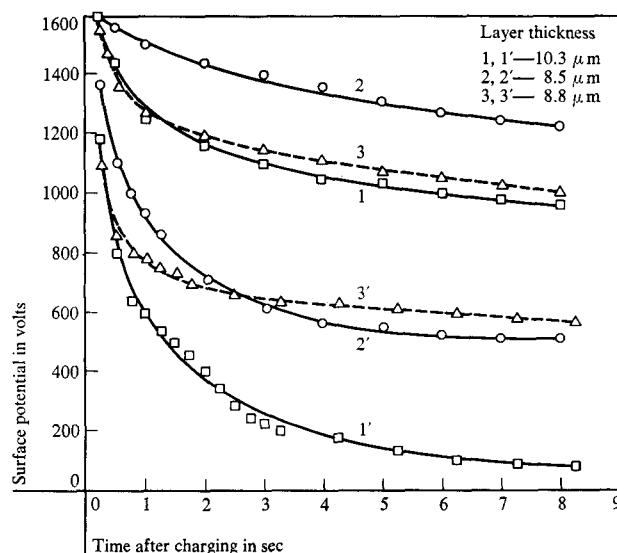


Figure 14 Dark decay curves for 1:1 TPC films on several different substrate metals. Negative (1) and positive charging (1') on aluminum; negative (2) and positive charging (2') on copper; and negative (3) and positive charging (3') on gold.

The positive charge acceptance for 1:1 TPC layers on unanodized aluminum substrates is usually relatively poor, as can be seen from Fig. 13. Here the charge acceptance, for both positive and negative charging, is plotted as a function of TNF concentration [1]. It is interesting to note that unsensitized polyvinylcarbazole has a good charge acceptance for positive charging and a rather low charge acceptance for negative charging. As the TNF concentration increases, the positive charge acceptance decreases, and the negative charge acceptance increases. The cross-over point for the two curves occurs at a TNF concentration (molar ratio) of about 0.06. At the optimum sensitivity concentration (1:1 TNF/PVCz) the negative charge acceptance has increased, and the positive charge acceptance has dropped to a very low value.

It is known that the nature of the substrate surface plays an important role in charge acceptance and other electrophotographic properties of photoconductive coatings. Recent experiments show that positive charge acceptance for the 1:1 TPC can be increased to a level comparable to that for negative charging by providing the proper barrier conditions at the substrate-photoconductor interface.

• Dark decay

Retention of surface charge on a photoconductive insulating layer in the dark is in many ways related to charge acceptance. The rate at which a charged electrophotographic plate loses its charge in the dark is referred to as the *dark decay rate*.

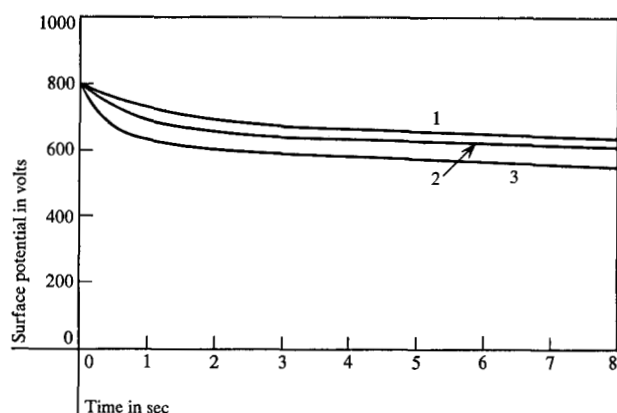


Figure 15 Effect of charging rate on negative-charge dark decay of 1:1 TPC (1) 8 in./sec; (2) 16 in./sec; (3) 32 in./sec.

Typical dark decay curves for 1:1 TPC films with positive and negative charging are shown in Fig. 14. The samples were coated on three different substrates: aluminum, copper and gold. It is evident that the use of copper and gold markedly decreases the dark decay rate for positive charging while the effect on negative charging is less pronounced. The aluminum used here was the metal side of aluminized Mylar.*

Corona charging rates and variations in charging techniques will influence the dark decay characteristics of the 1:1 TPC. Figure 15 shows that an increase in the charging rate increases the initial dark decay rate. In this experiment the charging rates are proportional to the speeds at which the sample plate is moved relative to the corona unit, the corona voltage being adjusted to produce nearly equal initial potentials on the photoconductive plate.

The effect of intermittent or stepwise corona charging is shown in Fig. 16. It is evident that incremental stepwise charging reduces the initial dark decay rate. The results given in Figs. 15 and 16 are for negative charging.

• Light decay

The discharge of the surface potential of photoconductive insulating layers as a function of time in the presence of light is usually measured by an electrometer and recorded as an oscilloscope trace. Curves produced by such traces are often referred to as light-decay curves, which provide the basic information for the determination of photosensitivity in electrostatic imaging.

Typical light-decay curves for a 1:1 TPC layer are shown in Fig. 17 for a sample exposed to light in the middle region of the visible spectrum (546.1 μm). The lower sensitivity for positive charging is apparent when the two curves in Fig. 17 are compared, particularly when it is

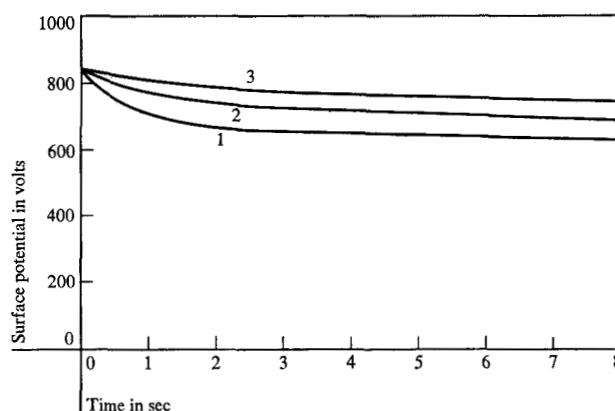
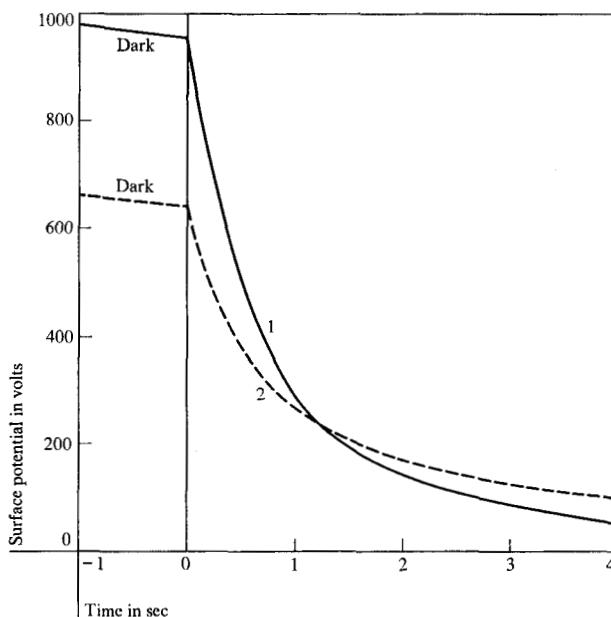


Figure 16 Effect of stepwise charging on negative-charge dark decay. (1) One step; (2) 3 steps 1 sec apart; (3) 8 steps 1 sec apart. Charging rate, 32 in./sec.

Figure 17 Typical light-decay curves for a 1:1 TPC sample. (1) Negative charge exposed to $3.02 \mu\text{W}/\text{cm}^2$; (2) positive charge exposed to $9.79 \mu\text{W}/\text{cm}^2$. $\lambda = 546.1 \text{ nm}$. Film thickness, $15 \mu\text{m}$.



recognized that the light intensity for positive charging is more than three times greater than for negative charging. The curve for positive charging starts at a lower initial potential than the curve for negative charging. This is due to a lower charge acceptance for positive charging for this 1:1 TPC sample.

• Photosensitivity

Methods for obtaining quantitative values for photosensitivity of electrostatic image-forming photoconductors from light decay curves have been discussed in a previous

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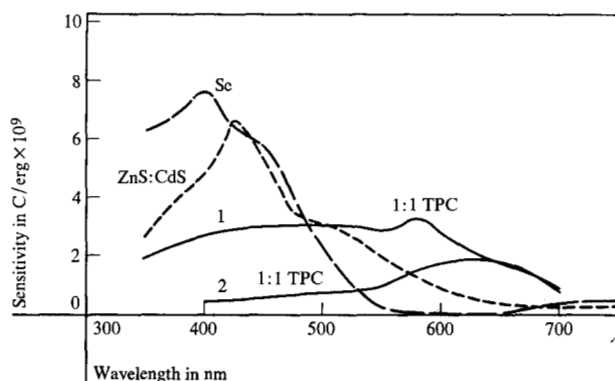


Figure 18 Spectral sensitivity of 1:1 TPC (20 μm) compared to amorphous Se (50 μm) and ZnS:CdS (25 μm ; 70% CdS). Curve 1, negative charging; curve 2, positive charging.

publication [12]. A common method is to use the reciprocal of the decay time to one-half the initial surface potential as a relative measure of sensitivity to a given light source. While this method provides a simple means of comparing photosensitive coatings for practical usage, it can produce misleading results when used to compare films of different spectral responses, different thicknesses and different dielectric properties.

Another method, which is useful in comparing a wide range of electrophotographic photoconductors, involves selecting a constant value of surface charge contrast [13] as a standard condition for all sensitivity determinations. The photosensitivity can then be computed in terms of the actual amount of charge dissipated per unit of incident light energy, e.g., coulombs per erg. This method requires determining the capacitance of a photoconductive layer, as well as obtaining its light-decay curves.

Spectral sensitivity. Figure 18 shows photosensitivity as a function of wavelength for the 1:1 TPC with data on amorphous selenium† and a ZnS:CdS binder plate [14] (30% ZnS, 70% CdS) included for comparison. The 1:1 TPC with negative corona has a nearly flat response throughout the visible region of the spectrum. While its sensitivity at 400 nm is only about one-third that of selenium, its over-all response to tungsten lamps and other white-light sources is nearly equivalent to selenium.

The sensitivity of 1:1 TPC for positive charging is considerably less than for negative charging, as can be seen by comparing curves 1 and 2 in Fig. 18. The response for positive charging (curve 2) shows a broad peak in the long-wavelength region at about 635 nm. The increased response in this region is probably due to greater light penetration into the layer, which permits photocon-

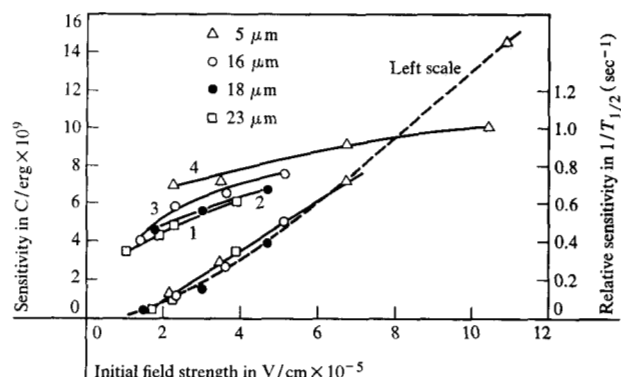


Figure 19 Sensitivity vs initial field strength for several samples of 1:1 TPC having different thicknesses. Electrostatic contrast of $3.5 \times 10^{-8} \text{ C/cm}^2$ used for equal charge decay (left scale); $V_0/2$ used for $1/T_{1/2}$, curves 1, 2, 3 and 4 (right scale). $\lambda = 404.5 \text{ nm}$.

duction of electrons from deep within the layer toward the positive charge on the surface.

The sensitivity units in Fig. 18 are given in terms of the amount of surface charge dissipated per unit of incident light energy (C/erg) for a surface charge contrast of $3.5 \times 10^{-8} \text{ C/cm}^2$.

Sensitivity vs field strength. Sensitivity of the 1:1 TPC increases rather markedly with field strength when computed on the basis of a constant electrostatic contrast. This is shown in Fig. 19, where sensitivity determined in this manner is plotted as a function of electric field strength for several 1:1 TPC coatings of different thicknesses. The increase of sensitivity with field is not so marked when the reciprocal of time for half potential drop is used as a sensitivity measurement (see curves 1, 2, 3 and 4, Fig. 19). When this method is used there is an apparent increase in sensitivity with a decrease in film thickness. However, when sensitivity is determined on the basis of a constant surface charge contrast, no thickness effect is indicated.

Quantum efficiency. The quantum efficiency (Q.E.) for effective discharge was defined for experimental purposes as the number of incident photons consumed per electron generated and conducted through the photoconductive film. Data obtained in this way for 1:1 TPC films are shown in Figs. 20, 21 and 22.

The spectral distribution of Q.E. (Fig. 20) shows a rather broad maximum at about 425 nm, falling off to lower values at both ends of the visible region. The data used in Fig. 20 were taken at a constant average field strength of $4.0 \times 10^5 \text{ V/cm}$.

The value of Q.E. depends rather strongly on field strength, as can be seen from Fig. 21. The Q.E. is more than quadrupled when the field strength is increased from

3.0×10^5 V/cm to 9×10^5 V/cm. The Q.E. is greater for a discharge of 3.5×10^{-8} C/cm² than for the initial decay, as shown in the Figure. This indicates a time-delay phenomenon at the onset of illumination.

Quantum efficiency and photosensitivity, computed from light-decay curves, both decrease with an increase in light intensity. This effect is shown in Fig. 22. The decrease is not great since an increase of nearly two orders of magnitude in light intensity reduces the photosensitivity and the Q.E. by about one-half. It has been observed, however, that there is an after-effect in the decay of surface potential after exposure, which results in a continued decay after illumination is stopped. This continued decay is greater for higher intensities. In practice, therefore, the decrease in sensitivity with light intensity is more or less compensated by this after-effect and no appreciable reciprocity failure is observed.

Response to flash exposure. Experimental results indicate that charge decay of 1:1 TPC obtained by flash exposure can vary considerably, depending on flash intensity and the initial surface potential of the charged film. This variation is clearly indicated in Figs. 23 and 24. The data were obtained for a xenon flash. Charge decay was sensed with a transparent probe electrometer and recorded with an oscilloscope. The spectral range of the flash was narrowed to $5500 \text{ \AA} \pm 250 \text{ \AA}$. The maximum energy impinging on the photoconductive layer was 73 ergs/cm^2 (2×10^{13} photons/cm²). This value was reduced in steps with neutral density filters. Duration of the flash was $3 \mu\text{sec}$. The photoconductor sample was $12.9 \mu\text{m}$ thick. Capacitance was calculated to be $1.85 \times 10^{-10} \text{ F/cm}^2$. The data in Fig. 23 are the final residual surface potentials after the flash exposures.

It is apparent from Fig. 23 that the discharge with flash exposure is essentially exponential. The point scatter in this figure is due primarily to difficulty in maintaining a constant initial potential for each flash series.

Figure 24 shows the amount of electrostatic contrast attainable with different combinations of initial potential and flash energy.

Quantum efficiencies for the case of flash exposure are shown in Fig. 25. Like the continuous-exposure data, Q.E. decreases with light intensity and increases with field strength. The data in Fig. 25 are not directly comparable to the analogous data of Figs. 21 and 22, since the wavelengths are different and the average light intensities for the $3 \mu\text{sec}$ flash are many orders of magnitude greater than those used in the case of continuous exposure.

• Electrostatic sensitometry

Representative sensitometric curves for the 1:1 TPC are shown in Figs. 26 and 27. The curves are given in terms of the surface potential as a function of image density,

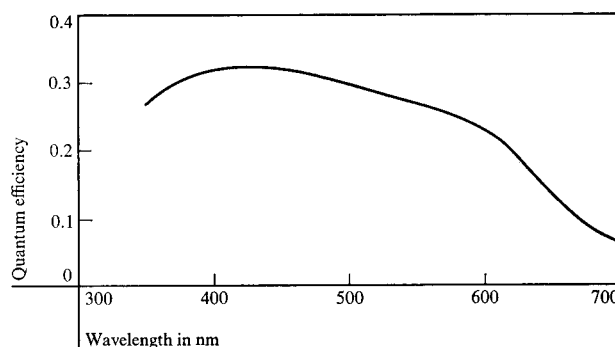


Figure 20 Quantum efficiency vs wavelength for the 1:1 TPC at a constant field strength of 4.0×10^6 V/cm.

Figure 21 Quantum efficiency vs field strength. Samples and conditions are the same as for Fig. 19. Solid line: Q.E. for initial discharge vs initial field; Broken line: Q.E. for discharge of 3.5×10^{-8} C/cm² vs average field strength.

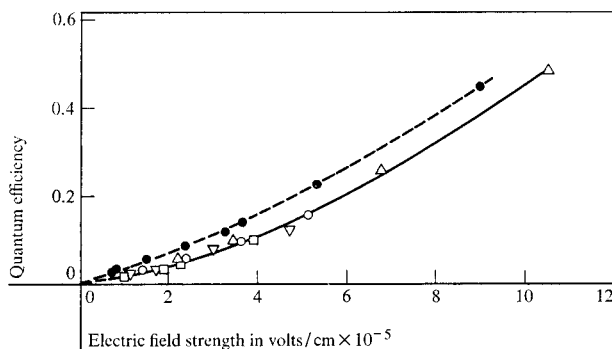
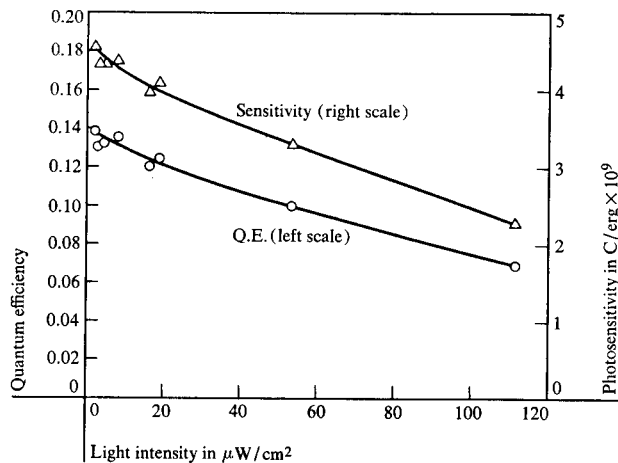


Figure 22 Effect of light intensity on quantum efficiency and photosensitivity of 1:1 TPC. $\lambda = 404.5 \text{ nm}$; electrostatic contrast = 3.5×10^{-8} C/cm²; average field strength = 4.5×10^5 V/cm.



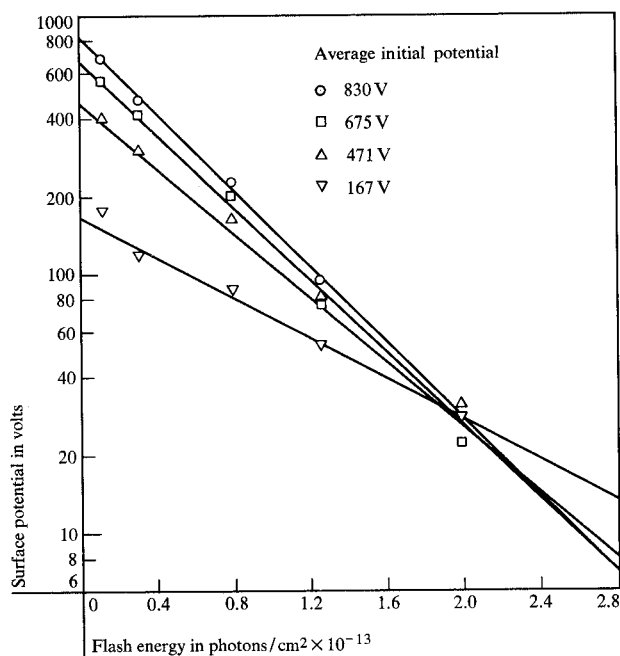
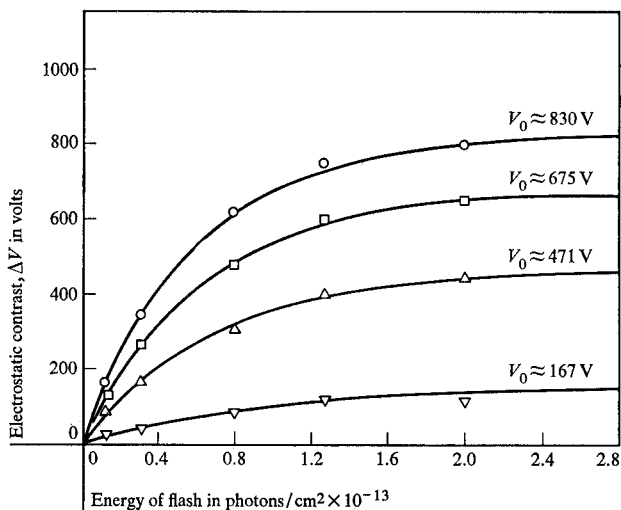


Figure 23 Charge decay of 1:1 TPC with flash exposure of 3 μsec at 550 μm .

Figure 24 Electrostatic contrast vs flash energy for 3 μsec flash at different initial potentials.



D. The light used was a tungsten filament lamp operating at 3000°K. Maximum intensity (I_0) incident on the photoconductor was 655 $\mu\text{W}/\text{cm}^2$. Surface potential was measured at a time after exposure corresponding to arrival of the exposed area at a developing station.

Curves for three different dark potentials are shown in Fig. 26. An increase in dark potential increases the slope (gamma) of the sensitometric curves and also increases electrostatic contrast.

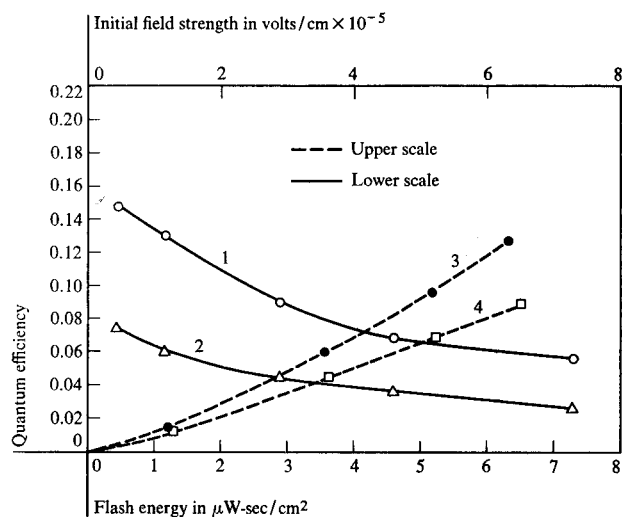


Figure 25 Quantum efficiency of 1:1 TPC with flash exposure, showing effects of electric field and flash energy. 3 μsec flash at 550 nm. With curves 1 and 2, initial fields are 6.4×10^5 and 3.6×10^5 V/cm, respectively. With curves 3 and 4, flash energies are 1.15 and 2.9 $\mu\text{W-sec}/\text{cm}^2$.

Figure 26 Electrostatic sensitometry of 1:1 TPC at different dark potentials.

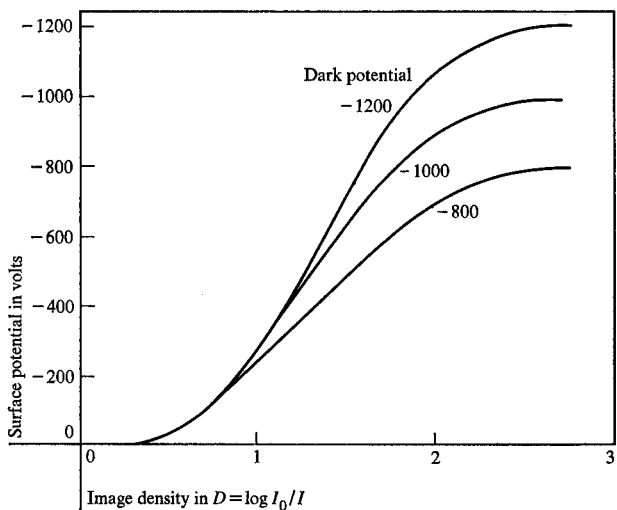


Figure 27 shows sensitometric curves for different exposure times. These curves are almost identical in shape and are displaced to the right by about 0.3 points on the density scale for each doubling of the exposure time. This indicates no appreciable reciprocity failure within this range of exposure times. In further tests reciprocity was found to hold fairly well with even shorter exposure times of 0.035 and 0.0155 sec.

Reciprocity characteristics for exposure of the 1:1 TPC

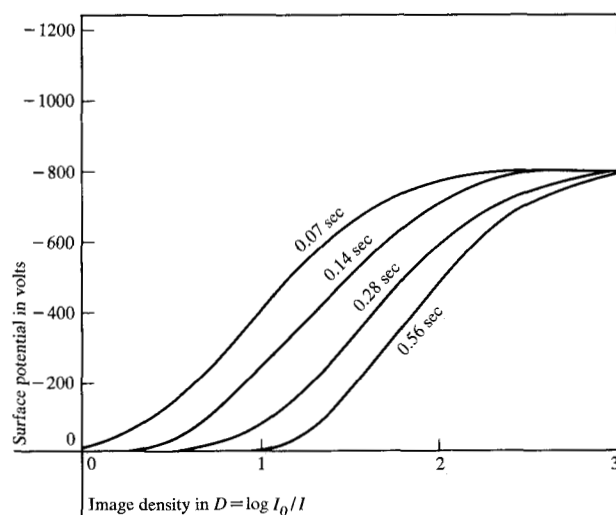


Figure 27 Electrostatic sensitometry of 1:1 TPC at different exposure times.

to a broadband light source peaking at 450 nm are shown in Fig. 28. It is apparent that reciprocity is rather good through a range of exposures from 3 μ sec to 1 sec.

In general the latitude of the 1:1 TPC is quite good. The sensitometric curves are linear over an image density range of 1.0 and the total usable range extends to about 2.0. While a change in the dark potential does not affect the latitude, it does provide a means of regulating the gamma. With this capability for changing the gamma, combined with a broad exposure latitude, it should be possible to use the 1:1 TPC to reproduce the tonal gradations required for good halftone and continuous tone pictures in an electrostatic imaging system provided with a suitable grey scale developing unit.

The above results are for negative charging of 1:1 TPC. Experiments with positive charging have shown that the shape of the sensitometric curves are about the same as for negative charging. However, because of rapid dark decay with positive charging for the samples tested, measurements were limited to exposure times of less than 0.35 sec.

• Humidity effects

Experiments indicate that relative humidity has no adverse effects on charge acceptance of 1:1 TPC films. However, there is a decrease in effective sensitivity of about 18 percent when the RH is increased from 20 to 70 percent. This is shown in Fig. 29, where sensitivity is given in terms of the reciprocal of light energy in microjoules/cm² required for a 300-volt drop from the initial potential using a tungsten light source. The reason for this change in effective sensitivity with relative humidity is not apparent. It is possible that the effect may be due to some change in the

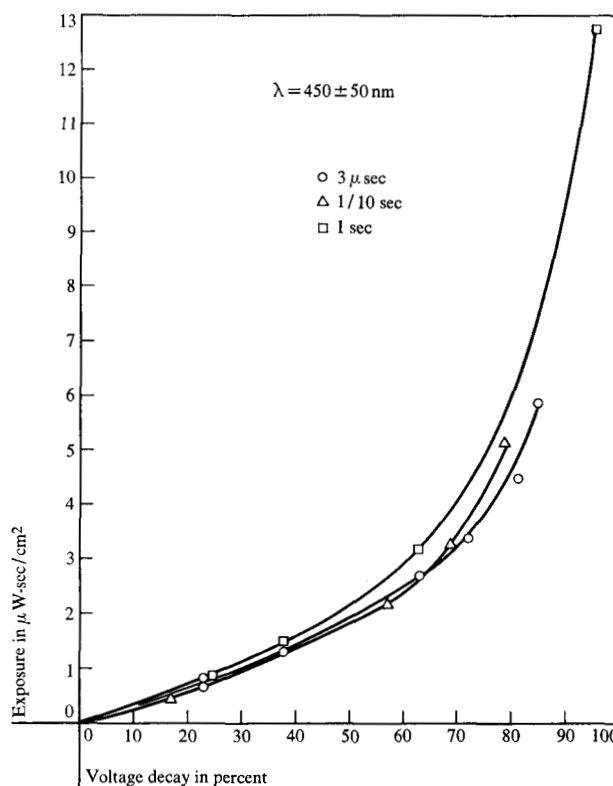
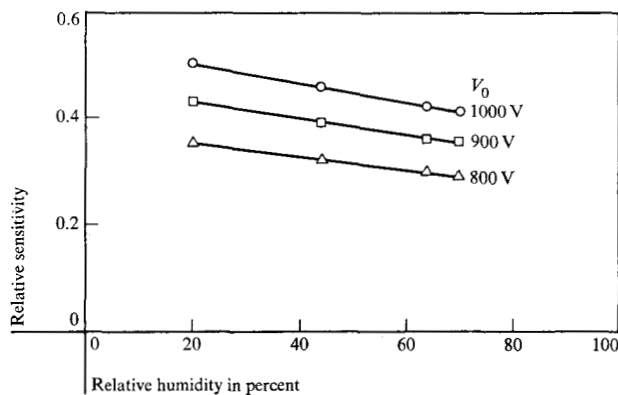


Figure 28 Decay of surface potential vs exposure for 1:1 TPC at three different exposure times.

Figure 29 Effect of relative humidity on the photosensitivity of 1:1 TPC at different initial potentials. Light source was tungsten.



experimental apparatus rather than in the photoconductive material.

Photogeneration of carriers in 1:1 TPC

Experiments on the photoinduced discharge of corona-charged 1:1 TPC plates indicate that some kind of activation energy is involved in the photogeneration of free charge carriers in this material.

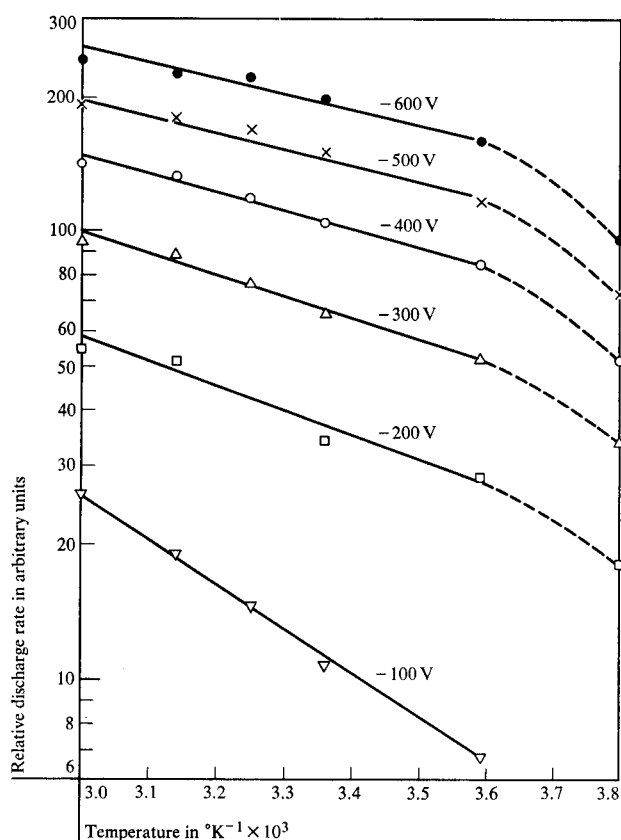
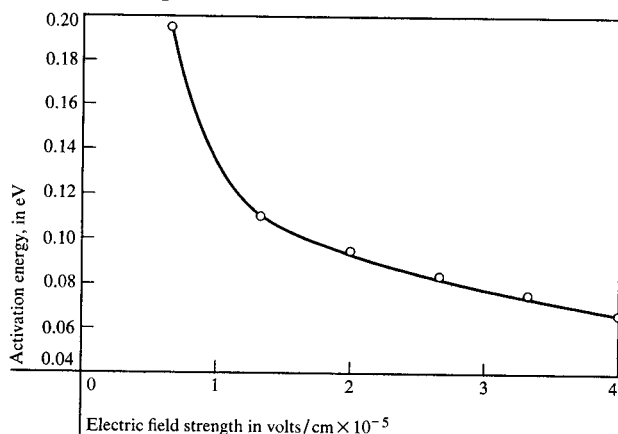


Figure 30 Effect of temperature on discharge rate of a 1:1 TPC plate at different surface potentials.

Figure 31 Activation energy as a function of field strength for a 1:1 TPC photoconductor.



Photodischarge curves were obtained on a 1:1 TPC sample charged to various initial potentials and maintained at temperatures ranging from -8 to $+65^{\circ}\text{C}$. These curves were used to determine discharge rates at various surface potentials along each curve. Strongly absorbed light (404.5 nm) was used to insure that charge

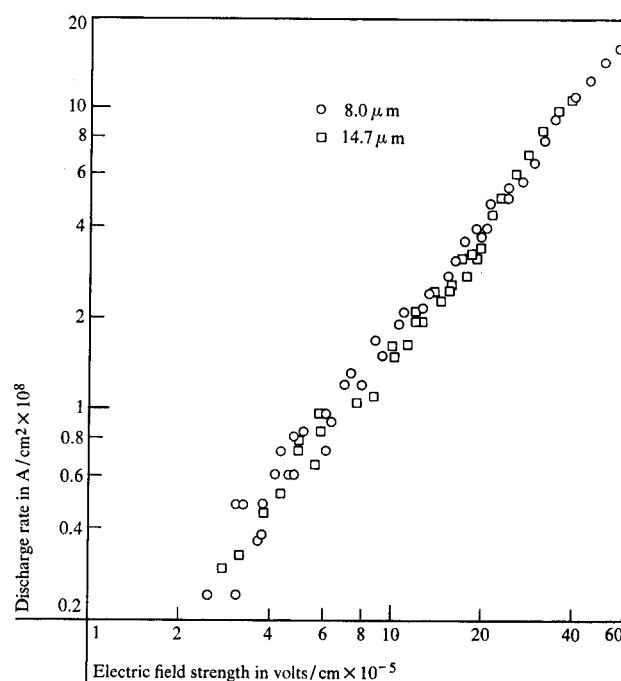


Figure 32 Photoinduced discharge rate as a function of field strength for two 1:1 TPC samples of different thicknesses. Light intensity = $2.49\text{ }\mu\text{W}/\text{cm}^2$. $\lambda = 404.5\text{ nm}$.

carriers moved through unilluminated media during the major portion of their trip through the photoconductive layer. Averaged discharge rates obtained in this manner are plotted as a function of reciprocal temperature in Fig. 30.

Except for the values at -8°C , the data approximate straight lines on the semilog plots. It has been suggested that the deviation from a straight-line relationship for the data at -8°C may be due to a phase transition in the film.

Activation energies computed from the straight-line portions of the curves of Fig. 30 are shown in Fig. 31, where they are plotted as a function of electric field strength. It is apparent that the activation energy decreases rather appreciably with field strength, but tends toward a constant value at high fields. The mechanism for this activation energy is not known. However, a field-dependent photogeneration of carriers is clearly indicated.

Field-controlled photogeneration of carriers is also indicated by the effect of electric fields on quantum efficiencies (see Figs. 21 and 25). Here we consider photogeneration to be the total process of primary excitation and recombination, i.e., the process of producing free carriers.

Light-decay curves for the 1:1 TPC show no residual potentials, but decay to near zero under continuous exposure even with strongly absorbed light. This indicates that there are no deep hole or electron traps in these

layers. Further evidence that electrons are not range limited is shown in Fig. 32, where the photoinduced discharge rate is plotted as a function of electric field strength for samples of two different layer thicknesses. Within experimental error the data are superimposed, indicating no thickness effect. The data were taken from light-decay curves obtained by exposing negatively charged films to monochromatic radiation at 404.5 nm. Analogous data for positive charging were not obtained.

The data at hand are not sufficient to warrant any attempts to propose a precise phenomenological model for the photoconductivity of the 1:1 TPC. Experiments now under way are directed toward acquiring a better understanding of the basic photoelectrostatic phenomena peculiar to this new photoconductive material.

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