ELECTROPHOTOGRAPHIC PERFORMANCE OF PHTHALOCYANINE PIGMENT COMPOSITES CONTAINING TITANYL PHTHALOCYANINE

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Abstract: Spectral sensitivity is an important consideration in photoconductor formulation, depending on the particular type of electrophotographic device in which it is used. High sensitivity in both the near-IR and visible spectral regions would be desirable for a photoconductor to be used with a wide variety of exposure sources. One possible way to achieve this goal is to use a mixture of charge generation pigments with absorptions in the desired spectral regions. The phthalocyanine pigments are well known for their use as charge generation materials in organic photoconductor (OPC) formulations. The absorption spectra (and the spectral sensitivity) of these pigments vary according to the metal coordinating the phthalocyanine, and with coordination of different axial ligands (O^{2-}, Cl^-, OH^-, et.al.). In this paper, phthalocyanine pigment composites with different sensitometric properties are prepared by coprecipitation of titanyl phthalocyanine with another phthalocyanine pigment from an organic solvent/trifluoroacetic acid solution. The phthalocyanine pigments used in the composites were chosen on the basis of their structures relative to titanyl phthalocyanine (i.e., presence or absence of an axial ligand). The initial electrophotographic performance of the composites is measured, and compared with the pure components prepared in similar fashion. The sensitivity of the photoconductor can be varied in a systematic fashion by varying the composition of the composite, and the composites show enhanced sensitivity when compared to mixtures of the component pigments.

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Introduction

In development of new organic photoconductor (OPC) materials, high photosensitivity is a key functional consideration, driven by the increased printing speed of electrophotographic engines. In a schematic of a typical two-layer photoconductor system shown in Figure 1:

## Figure 1 -- Photogeneration and Charge Transport in a Typical Two-Layer OPC
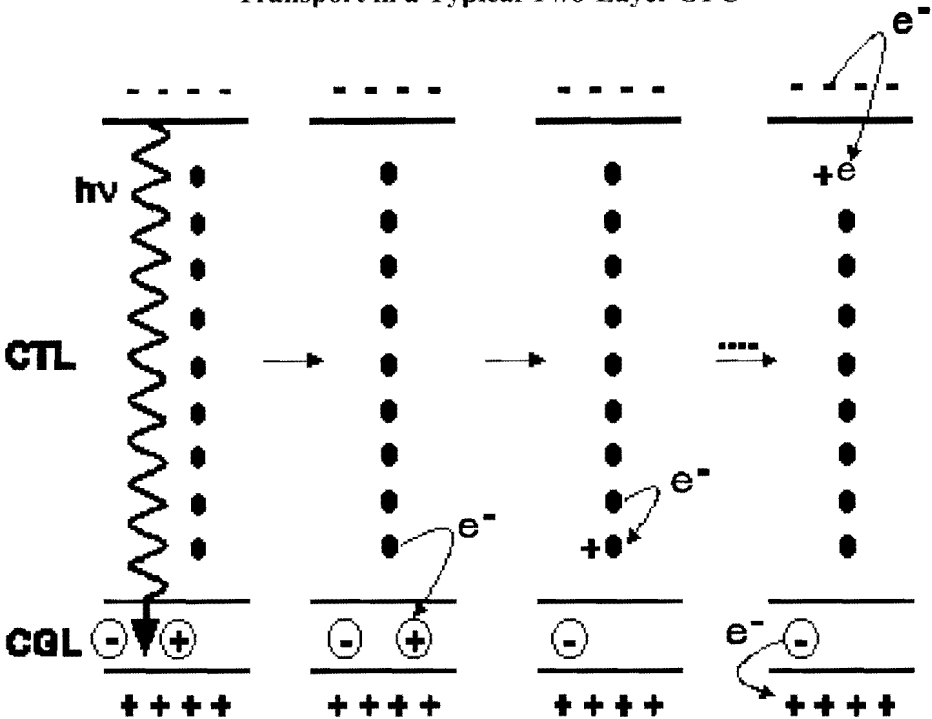
light is absorbed in the charge generation (CG) layer, giving rise to a photogenerated hole-electron pair. Depending on the whether the system is charged positive or negative, a electron or hole is injected into the charge transport (CT) layer and migrated to the surface where it neutralizes the initial charge and gives rise to a latent image. The sensitivity of the photogeneration process is affected by a number of factors. Among these are the electronic structure of the charge generation pigment, and its crystal structure and morphology.

The phthalocyanines are a well-known class of charge generation pigments. Their use in photoconductor formulations has been reviewed by Law (1993) and Hanack (1990). Specific phthalocyanines such as titanyl phthalocyanine [O=Ti(pc)] have been claimed to give photosensitivities (expressed as $E_{1/2}$, which is the energy required to bring the photoconductor to half of its original charge voltage) of < 0.2 mJ/cm^2 (Fujimaki, 1990). Similarly high sensitivities have also been claimed for vanadyl phthalocyanine [O=V(pc)]

(Loutfy, 1988) and hydroxygallium phthalocyanine [HO-Ga(pc)] (Daimon, 1994; Hsiao, 1994; Mayo, 1994). Each of the pigments have the same basic molecular structure (Figure 2) where a metal is coordinated to the phthalocyanine ligand, and the metal is also coordinated by an electronegative axial ligand. It has been postulated that the enhanced sensitivity shown by these metal phthalocyanine complexes is a result of enhanced intermolecular interaction, brought about unidirectional orientation of the M-X bond (Enokida, 1990; Hiller, 1982), or by the alignment of transition moments in the crystalline pigment, which can occur in metallated **or** non- metallated phthalocyanines (Oka, 1993a; Oka, 1993b).

Figure 2 -- Molecular Structure of X-M(pc)
X=axial ligand, M=coordinating metal
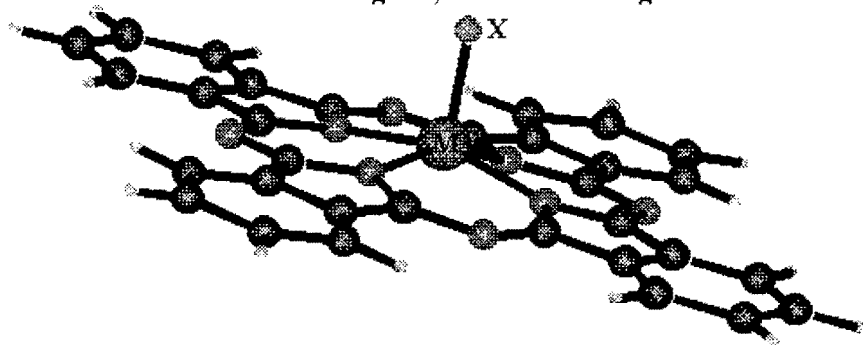
Spectral sensitivity is also a key factor in the development of new charge generation pigments. Significant absorption in the near-IR is necessary for use with typical semiconductor laser sources, but sensitivity in the visible region is also required for exposure with broadband light sources (i.e., copier OPC applications). To obtain a photoconductor with sensitivity across a wide spectral range, mixed-pigment CG formulations have been employed. Several approaches have been used to prepare these formulations, including combination of dissimilar pigment types (Saito, 1993; Suzuki, 1992; Loutfy, 1989; Anayama, 1988), and combining pigments of similar structure by physical means or by dissolution and coprecipitation of pigment mixtures (Hayashida, 1993; Itami, 1992; Kazmaier, 1992a; Kazmaier, 1992b; Nukada, 1992; Enokida, 1989). Although the insolubility of many pigments (particularly the phthalocyanines) makes pigment coprecipitation challenging, it may offer the greatest opportunity to control the crystalline structure of the composite pigment, particularly when the component pigments are nearly isostructural.

In this study, the initial premise was to start with a charge generation pigment, titanyl phthalocyanine, which is very sensitive in the near-IR. Chloroindium phthalocyanine [ClIn(pc)] is another in the series of metallated phthalocyanines with an axial ligand, and whose electronic spectra differs noticeably from titanyl phthalocyanine. The charge generating properties of chloroindium phthalocyanine are well characterized (Loutfy, 1987; Loutfy, 1985), and some studies of the initial electrical properties of O=Ti(pc)/ClIn(pc) composites have

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already been carried out (Hayashida, 1994). In our study, the properties of the O=Ti(pc)/ClIn(pc) composite are contrasted with a O=Ti(pc)/ H$_2$(pc) composite. Here, the second component does **not** possess an axial ligand, and intermolecular interaction should be reduced; the sensitivity of this composite should be reduced as well, if intermolecular interaction indeed plays a role in determining the sensitivity of the CG pigment. If another factor such as transition moment alignment (which is not dependent on the presence of an axial ligand) is dominant in determining the photosensitivity, then the H$_2$(pc) and ClIn(pc) composites should exhibit similar performance. As a prelude to measurement of their spectral sensitivity in an electrophotographic evaluation, the spectral properties of the composites were studied and observations made regarding the structures of the composites vs. the component pigments.

Experimental

General methods. All solvents used in synthetic procedures or composite preparation were reagent grade or higher, and were used as supplied by commercial sources. Phthalonitrile (98%) and titanium (IV) isopropoxide (97%) were used as supplied by Aldrich. Indium trichloride (99+%) was used as supplied by Alfa Aesar/Johnson Matthey. Anhydrous ammonia was used as supplied by Matheson Gas Products, Inc. X-form "metal-free" phthalocyanine [H$_2$(pc)] used as a CG pigment was electrophotographic grade and was used as supplied by Zeneca Specialties. Hole transport materials used in the photoconductor charge transport formulations included 4-(diethylamino)-benzaldehyde diphenylhydrazone (DEH) and tri(p-tolyl)amine (TTA). These materials were electrophotographic grade, and were used as supplied by Eastman Chemical and Zeneca Specialties respectively. Binder materials for the photoconductor formulations included polyvinylbutyral as the charge generation binder, bisphenol-A polycarbonate and a bisphenol-A/bisphenol-TMC copolycarbonate (TMC=3,3,5-trimethylcyclohexylidene) as the charge transport binders; these materials were used as supplied. Elemental analyses were obtained from E&R Microanalytical Laboratory, Corona, NY. UV-visible spectra of thin-film and solution samples were obtained on a Varian Cary 3 spectrophotometer.

Characterization of the photoconductor samples was carried out on a Lexmark-built electrophotographic parametric tester. The exposure source for the tester was a 780 nm gallium arsenide laser, with exposure energy ranged from 0.0-2.0 mJ/cm^2. Photoconductor charging was carried out via a charge corona, and discharge voltages were measured by Trek electrostatic probes at 524 milliseconds after exposure. A constant temperature chamber was used to house the test engine to ensure isothermal conditions during the measurements.

Synthesis. Standard Schlenk techniques were used to handle air- and/or moisture-sensitive reagents. 1,3-diiminoisoindoline (DII) was prepared by a previously described method (Lowery, 1965) from reaction of phthalonitrile with anhydrous ammonia in methanol solution. Metal-substituted phthalocyanines

were prepared by modification of standard methods (Lowery; Shaposhnikov, 1977). In a typical synthesis of titanyl phthalocyanine, N,N-dimethylaniline (DMA;1700 ml, 99%) was used as the reaction solvent and was degassed for 30 minutes with nitrogen. 1,3-diiminoisoindoline (148.00 g; 1020 mmol) was added to the solvent, titanium isopropoxide (76 ml; 255 mmol) was added to the reaction mixture by syringe under positive nitrogen pressure, followed by heating to 70-80∞C. Isopropanol formed in the reaction was distilled into a Dean-Stark trap, then the temperature of the mixture raised to 170∞C. After 12 hours, the reaction mixture was cooled to ca. 80∞C, and the crude product (a deep purple solid) filtered from the hot DMA solution. After washing the product with fresh DMA, the solid was resuspended in a second aliquot of solvent and heated to 170∞C. After 12 hours, the suspension was cooled to ca. 80∞C, and the solid filtered off. The solid was then washed with methanol, and a similar washing procedure carried out (methanol reflux). The purified product is analytically pure, and suitable for electrophotographic purposes; yield = 117.23 g (80%). The procedure is identical for chloroindium phthalocyanine, except that indium (III) chloride is used as the source of the Cl-In fragment.

Composite preparation. Titanyl phthalocyanine and chloroindium phthalocyanine were dissolved in methylene chloride/trifluoroacetic acid solution (for example, see Duff, 1991 and Duff, 1992). Typically, 16.00 g of pigment was dissolved in 160 ml methylene chloride/trifluoroacetic acid (80:20 by volume). Metal-free phthalocyanine was not as soluble in this solvent pair, so a cosolvent in addition to methylene chloride was employed. In this case, 16.00 g $H_2(pc)$ was dissolved in a mixture of 160 ml trifluoroacetic acid, 256 ml methylene chloride, and 256 ml acetonitrile. The phthalocyanine containing-solutions were then precipitated from a tenfold excess (by volume) of a 1:1 methanol/water or ethanol/water mixture. The composite pigments were prepared by mixing the component solutions together [in the case of $O=Ti(pc)/H_2(pc)$ composites, the $O=Ti(pc)$ solution was diluted by a factor of two to avoid precipitation of $H_2(pc)$], stirring for 5 minutes, and precipitating from the appropriate volume of alcohol/water. After precipitation, the solid pigments were centrifuged, and washed with water until the washings were completely neutral. The washed solids were rinsed with methanol, and dried under vacuum.

Photoconductor formulation. Phthalocyanine dispersions for charge generation coatings were prepared by adding 6.00 g of the reprecipitated phthalocyanine pigment and 3.00 g polyvinylbutyral to 150.00 g cyclohexanone, and milling with 2.0 mm glass beads on a paint shaker for 12 hours. The dispersion was then let down with 150.00 g methyl ethyl ketone, and milled for an additional 5 minutes. The CG formulation was coated onto an anodized aluminum drum using a dip coating process, and dried at 100∞C for 5 minutes. After cooling, the drum was then coated with a charge transport solution (20.0% total solids) containing a hole transport dopant (40%) and bisphenol-A polycarbonate or bisphenol-A/bisphenol-TMC copolycarbonate (60%) dissolved in tetrahydrofuran. The hole transport dopants used in this study were 4-(diethylamino)-benzaldehyde diphenylhydrazone (DEH) and tri(p-tolyl)amine (TTA). After dip-coating the transport solution onto the CG coating, the finished

photoconductor was dried at 100∞C for 1 hour. The drums were then stored at ambient conditions for at least 12 hours prior to electrical testing. Optical densities for the charge generation layer and coat weights for the charge transport layer were consistent for all coatings to allow direct sensitometric comparisons between formulations.

Results

Preparation of the $O=Ti(pc)/ClIn(pc)$ and $O=Ti(pc)/H_2(pc)$ composites were carried out as described (Duff, 1991, 1992; Kazmeier, 1992a, 1992b). These references describe the use of a methylene chloride/trifluoroacetic acid solvent system used to dissolve phthalocyanine pigments. Use of this solvent pair is preferred for several reasons in comparison to concentrated sulfuric acid, commonly used as a solvent for phthalocyanine "acid pasting" procedures. The solubility of many phthalocyanines is higher in CH_2Cl_2/TFA than in sulfuric acid, and the solvent pair is much more easily removed from the precipitated pigment. The relatively low acid concentration in the CH_2Cl_2/TFA solvent pair also reduces the risk of demetallation of the phthalocyanine, which is often observed in H_2SO_4 solution. Elemental analyses of ClIn(pc) precipitated from CH_2Cl_2/TFA (and $O=Ti(pc)/ClIn(pc)$ composites) show no evidence of demetallation, even when kept in solution over extended periods (> 1 hr.).

Individual phthalocyanine pigments have varied solubilities in CH_2Cl_2/TFA; in particular, $H_2(pc)$ has limited solubility in this solvent pair. A new observation from this study was that the addition of acetonitrile (CH_3CN) to the CH_2Cl_2/TFA solvent pair enhanced the solubility of $H_2(pc)$. This allowed the precipitation of $O=Ti(pc)/H_2(pc)$ composites from solutions of relatively high pigment concentration, simplifying the isolation of the solid composite.

The sensitivity of the composite OPC formulations varies depending on the nature of the hole transport dopant used in the charge transport layer. CG formulations containing $H_2(pc)$ inject most efficiently into DEH (hydrazone) transport layers. Conversely, formulations containing ClIn(pc) showed nearly equivalent electrical performance when formulated with either DEH or TTA (arylamine) transport layers. Since $O=Ti(pc)$ shows good sensitivity with either type of hole transport, any differences between the composite formulations must be related to electronic or structural changes between $H_2(pc)$ and ClIn(pc). The most likely explanation is that $H_2(pc)$, with its lower ionization potential (Schlettwein, 1994; Orti, 1992), only injects readily into the hole transport material (DEH) with lower ionization potential.

Voltage vs. energy curves for the $O=Ti(pc)/H_2(pc)$ CG pigment composites are shown in Figure 3. Each of these CG formulations was coated with a DEH-containing hole transport layer. For purposes of comparison, each of the curves has been normalized to a common initial charging voltage (voltage prior to laser exposure). As can be seen from the V vs. E curves, the sensitivities of the formulations vary over a relatively narrow range. In comparing the two "pure" CG formulations, the $O=Ti(pc)$ formulation has greater initial sensitivity

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than the $H_2(pc)$ formulation. The decreased sensitivity of the $H_2(pc)$ formulation is not a result of the acid pasting procedure; in fact, the sensitivity of the acid pasted $H_2(pc)$ pigment is improved vs. the untreated pigment. The sensitivity of the pigment composites also does not vary consistently with pigment composition. The sensitivity of the 3:1 $O=Ti(pc)/H_2(pc)$ composite is nearly identical with that of pure $O=Ti(pc)$, where the 1:3 $O=Ti(pc)/H_2(pc)$ composite is **less** sensitive than pure $H_2(pc)$.

In several previous studies, it has been postulated that the minority component of a pigment composite can be incorporated into the host lattice of the majority component. (Itami, 1991) The crystal structure of X-form $O=Ti(pc)$ produced by precipitation from CH_2Cl_2/TFA solution has not been determined, but the powder patterns of X-form $O=Ti(pc)$ and X-form $H_2(pc)$ are considerably different, indicating that the materials are not isomorphous. Further, powder patterns of X-form $H_2(pc)$ before and after dissolution in CH_2Cl_2/TFA are identical, showing that X-form $H_2(pc)$ can be produced by this precipitation process. The UV-visible spectrum of the $O=Ti(pc)/H_2(pc)$ composites, shown in Figure 4, show that the electronic structure of the 1:3 composite strongly resembles that of pure X-form $H_2(pc)$. If the $O=Ti(pc)$ is being incorporated into the X-form $H_2(pc)$ lattice in the 1:3 $O=Ti(pc)/H_2(pc)$ composite, then these results could indicate that the crystal structure for X-form $H_2(pc)$ is not suited for high generation efficiency with $O=Ti(pc)$. Study of the crystal structure of the composites (via X-ray powder diffraction) should help to clarify this point.

Differences between $O=Ti(pc)/H_2(pc)$ composites and $O=Ti(pc)/H_2(pc)$ mixtures are illustrated in Figure 5. The $O=Ti(pc)/H_2(pc)$ mixtures were prepared by milling the two components together during formulation rather than by the coprecipitation method used to prepare the composites. Again, these CG

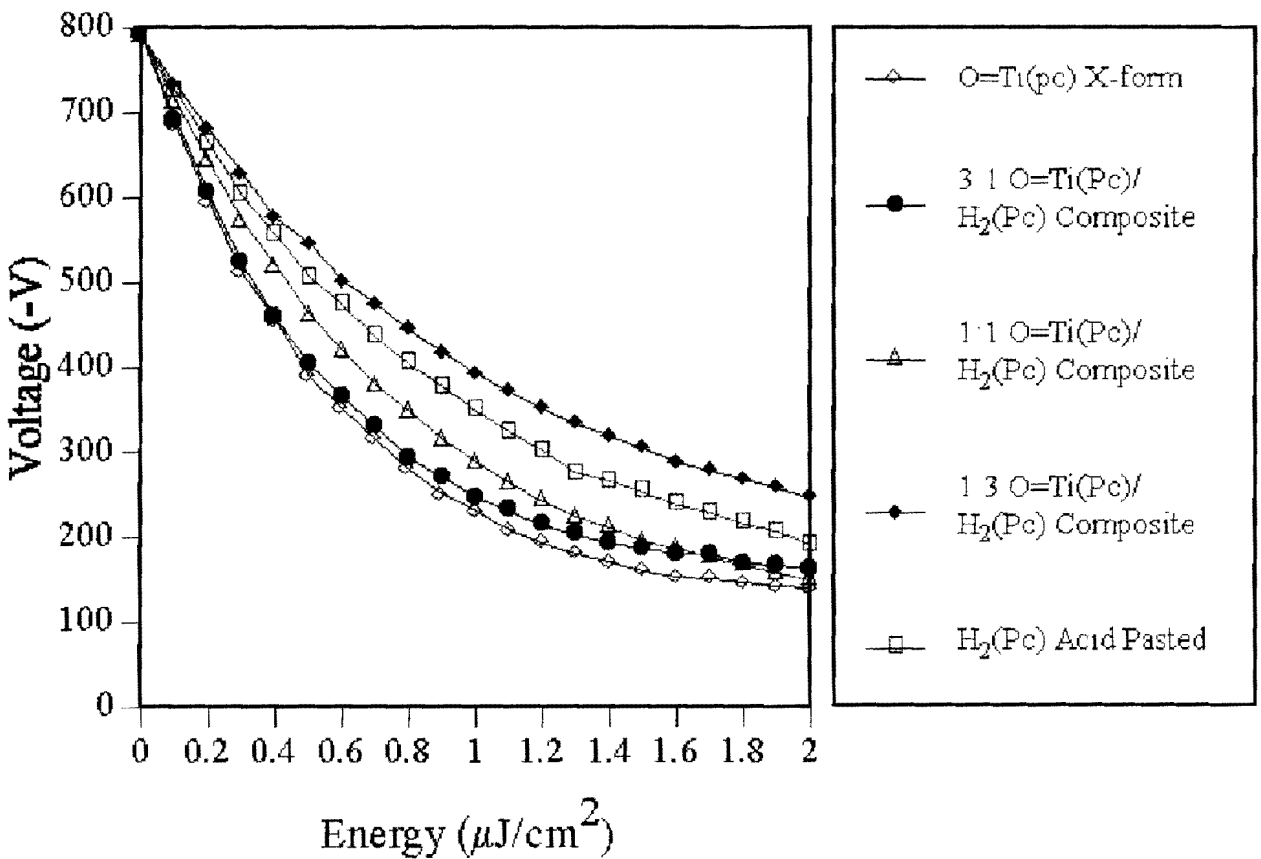Figure 3 – V vs. E: Composites of O=Ti(pc)/H$_2$(pc) [DEH transport]

Legend:
- O=Ti(pc) X-form
- 3 1 O=Ti(Pc)/ H$_2$(Pc) Composite
- 1 1 O=Ti(Pc)/ H$_2$(Pc) Composite
- 1 3 O=Ti(Pc)/ H$_2$(Pc) Composite
- H$_2$(Pc) Acid Pasted

Y-axis: Voltage (-V)
X-axis: Energy (μJ/cm^2)

Figure 4 -- Thin Film UV-Visible Spectra of O=Ti(pc)/H₂(pc) Composites

3:1 O=Ti(pc)/ H₂(pc) composite

1:1 O=Ti(pc)/ H₂(pc) composite
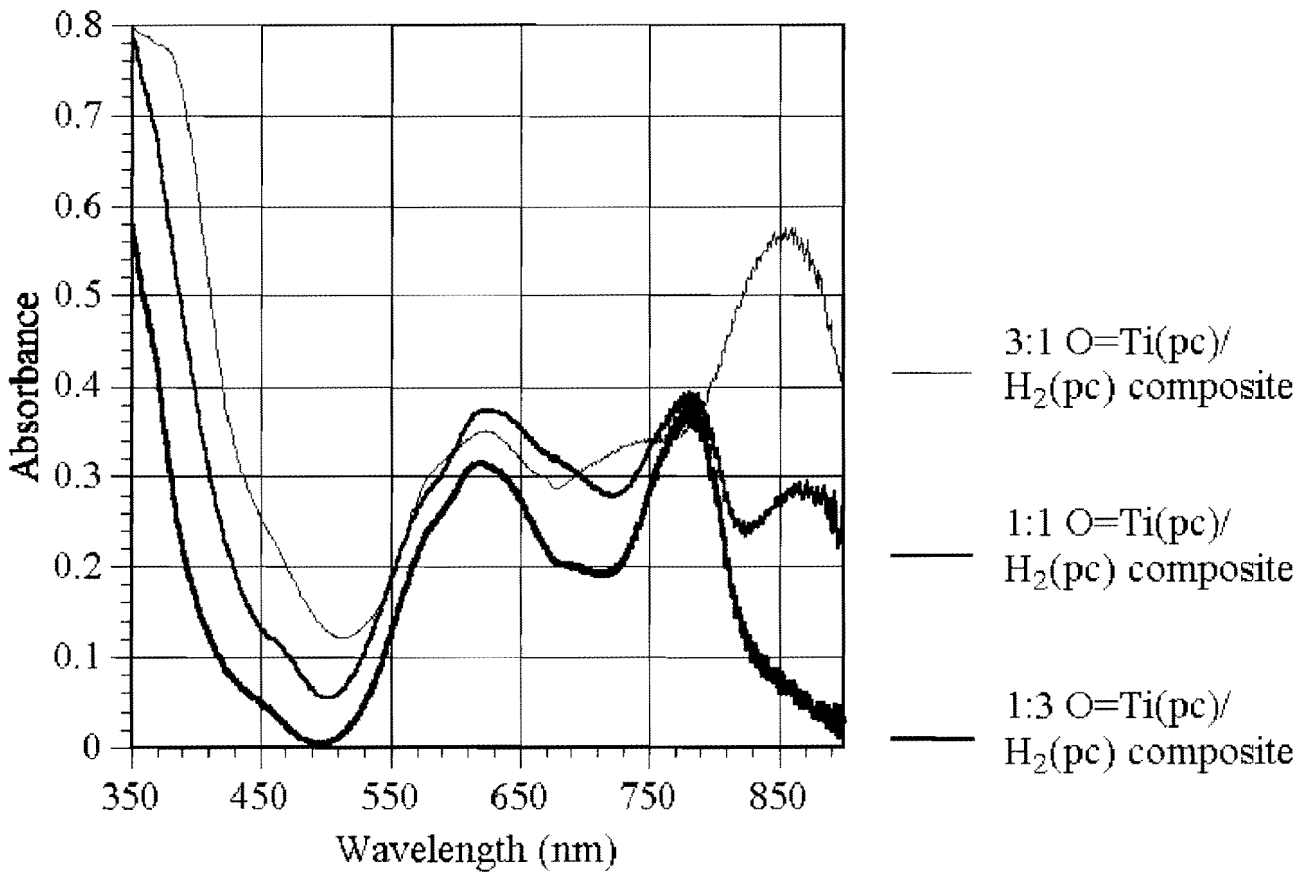
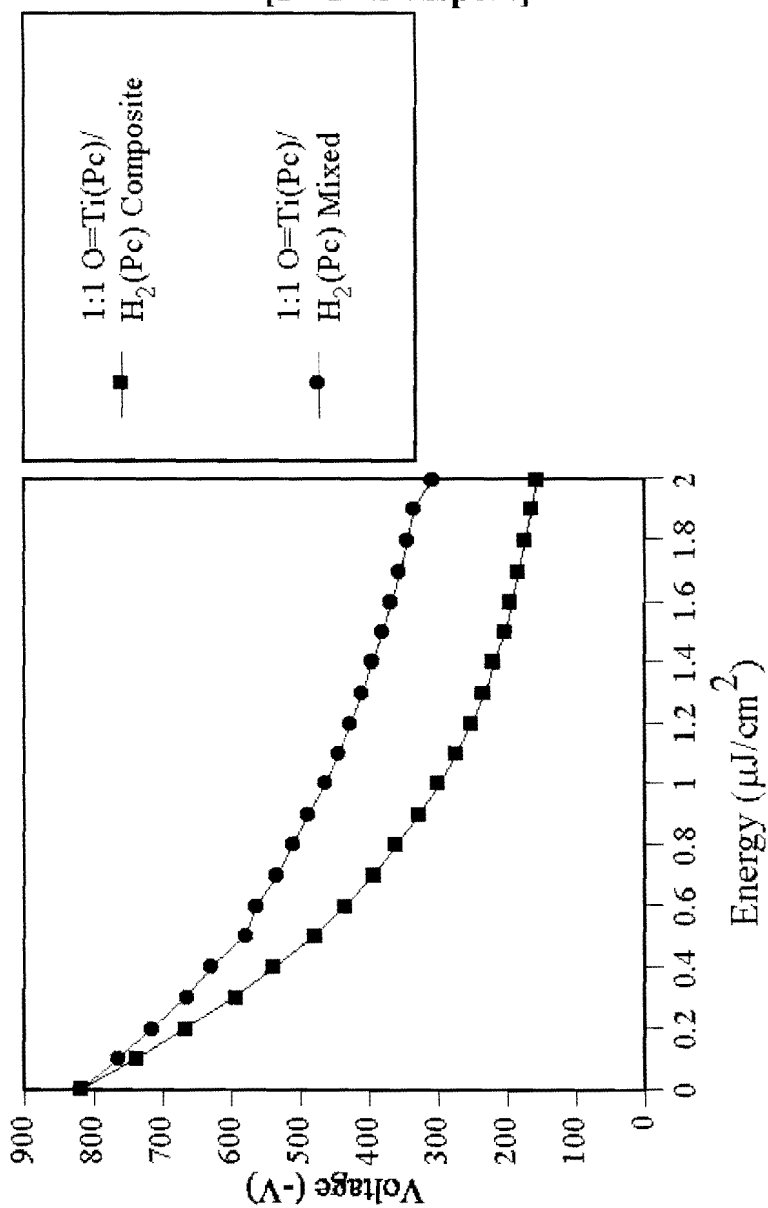1:3 O=Ti(pc)/ H₂(pc) composite

Figure 5 -- V vs. E: Composites and Mixtures of O=Ti(pc)/H₂(pc) [DEH transport]

composite formulations were coated with DEH-containing hole transport layers. The initial sensitivity of the composite is much greater than that of the mixture, along with giving a much lower residual voltage. The sensitivity of the formulation containing the $O=Ti(pc)/H_2(pc)$ mixture is even slightly lower than for a pure $H_2(pc)$ formulation. Previous studies of pigment composites prepared by codissolution have shown that single particles can be formed containing both components, where in a physical mixture of the two components, the single particles will contain only one component. Our results suggest a similar conclusion, although X-ray powder patterns of the composite and the mixture will be necessary to characterize structural differences between the two pigments.

Voltage vs. energy curves for the $O=Ti(pc)/ClIn(pc)$ CG pigment composites are shown in Figure 6 and Figure 7. Each of these CG formulations was coated with either a TTA-containing (Figure 6) or DEH-containing (Figure 7) hole transport layer. Relatively small changes in sensitivity are observed from pure $O=Ti(pc)$ to 1:3 $O=Ti(pc)/ClIn(pc)$ with either transport layer. A study of $O=Ti(pc)/ClIn(pc)$ composites precipitated from sulfuric acid solution (Hayashida, 1994) also shows very little change in sensitivity from a 90:10 to 50:50 ratio of $O=Ti(pc)/ClIn(pc)$. This correlates with their observation of only slight structural changes (by powder pattern) in this range of composition. Our powder pattern for the "pure" acid-pasted $ClIn(pc)$ matches that of the synthetic material (Loutfy, 1987), where the Hayashida study indicates a different polymorph prepared by sulfuric acid pasting. However, both sets of electrical data indicate that $ClIn(pc)$ can be incorporated into the $O=Ti(pc)$ lattice at high concentrations with minimal change in photosensitivity. The same conclusion may be true for $H_2(pc)$ at low concentrations in the composite, but as discussed earlier, at higher concentrations the structural change toward X-form $H_2(pc)$ leads to low photosensitivity.

Conclusions

Phthalocyanine pigment composites with different sensitometric properties have been prepared by coprecipitation of titanyl phthalocyanine $[O=Ti(pc)]$ with either "metal-free" phthalocyanine $[H_2(pc)]$ or chloroindium phthalocyanine $[ClIn(pc)]$ from an organic solvent/trifluoroacetic acid solution. The $O=Ti(pc)/ClIn(pc)$ composites show good sensitivity $(E_{1/2} < 0.6 \text{ mJ/cm}^2)$ with either a hydrazone- (DEH) or arylamine-containing (TTA) charge transport formulation. The $O=Ti(pc)/H_2(pc)$ composites only inject well into DEH transport formulations, attributable to an ionization potential mismatch between $H_2(pc)$ and TTA. It is also clear that mixtures of the two pigments show lower electrophotographic sensitivity than composites with the same pigment composition. Incorporation of the second pigment component into the $O=Ti(pc)$ lattice is obviously an important factor in obtaining a composite with high photosensitivity.

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Figure 6 -- V vs. E: Composites of O=Ti(pc)/ClIn(pc) [TTA transport]

Legend:
- ■ O=Ti(Pc) X-Form
- ○ 3:1 O=Ti(Pc)/ ClIn(Pc) composite
- ▲ 1:3 O=Ti(Pc)/ ClIn(Pc) composite
- — ClIn(Pc) Acid Pasted

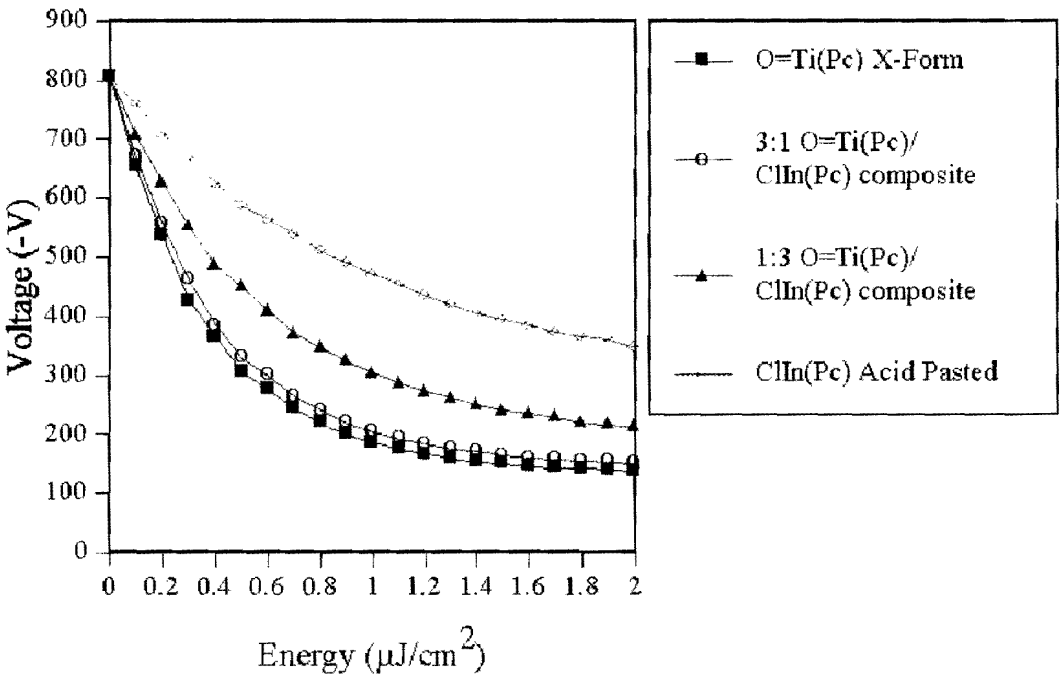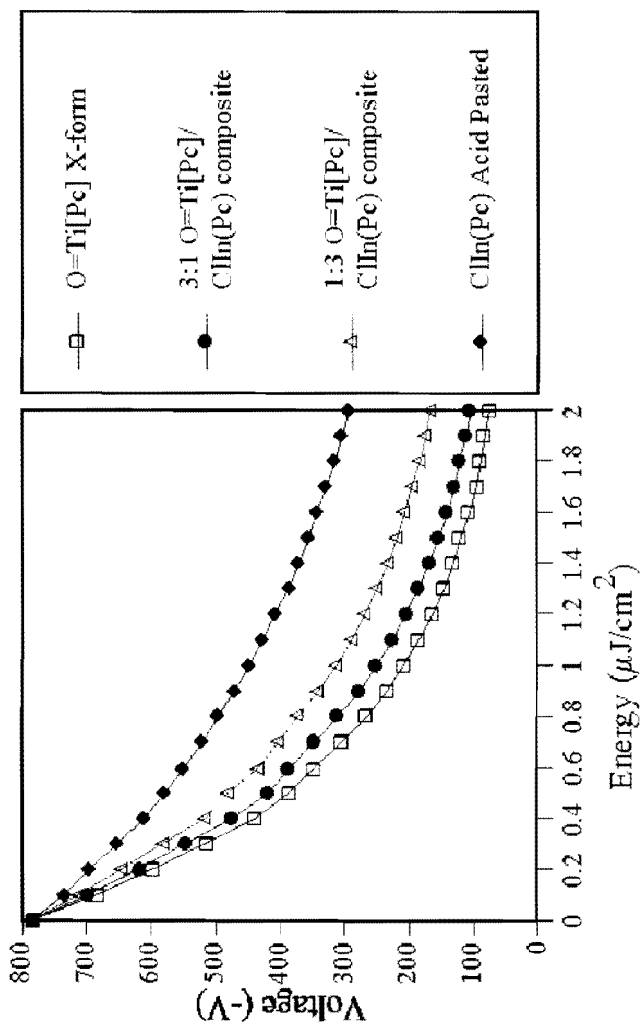Y-axis: Voltage (-V)
X-axis: Energy (μJ/cm^2)

Figure 7 -- V vs. E: Composites of O=Ti(pc)/ClIn(pc)

[DEH transport]

The O=Ti(pc)/ClIn(pc) CG pigment composites also show a narrow range of sensitivity for a relatively wide range of composition [from pure O=Ti(pc) to 1:3 O=Ti(pc)/ClIn(pc)]. The electrical data from these composites indicates that ClIn(pc) can be incorporated into the O=Ti(pc) lattice at high concentrations with minimal change in photosensitivity (at 780 nm). The O=Ti(pc)/H_2(pc) composites show a larger sensitivity range, consistent with a lower incorporation of H_2(pc) into the O=Ti(pc) crystal structure. X-ray powder diffraction studies of the composites will be necessary to fully characterize the structural changes in the composites. Spectral sensitivity measurements on the composites will also characterize the effect of the structural changes on the photosensitivity at different wavelengths, although the UV-visible spectra of the composites suggest that significant absorption will occur across the visible and near-IR regions.

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