Newtonian, Colloidally Stable, Ultrasonic-Insensitive Charge Generating Layer Dispersion Compositions with Instantly Tunable Photosensitivity

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Abstract

High-quality electrophotographic applications demand a photoconducting element that is "perfect" in many aspects:

1. *defect-free, almost to the submicrometer level,*
2. *environmentally insensitive, and*
3. *possessing a well-defined photosensitivity that matches the electrophotographic rendering process.*

The charge generation layer is typically coated from a preformed pigment dispersion. The stability, quality, and composition of that dispersion critically influence the production of that "perfect" photoconducting element.

This work describes the development of Newtonian, colloidally stable, ultrasonic-insensitive, charge generation layer dispersion compositions with instantly tunable photosensitivity. These dispersions enable robust photoconductor manufacturing processes and provide instantly accessible photospeeds ranging from 0.05 to 1.0 cm^2/ergs (500–100 V photodischarge).

Introduction

In a dual-layer photoconductor, the charge generation layer is the light-responsive element that captures the imaging information. Good image quality requires that the capture be complete and realistic. That is, we want to reproduce the image accurately without the introduction of artifacts. For high-quality applications such as digital printing, the charge generation layer uniformity needs to be high on both a micro and macro level. Pigment dispersions are the preferred charge generation layer materials. Those dispersions need to be stable with nanoparticle-sized distribution. Additionally, interlayer adhesion and controlled photo discharge are of paramount importance.

This paper describes the development of charge generation dispersions that fit all of the above requirements. Polyvinyl butyral polymers have been proven to be excellent binders for charge generation layer dispersions. In general, they provide very stable dispersions with very small particle size distribution. However, one important drawback is the very poor interlayer adhesion. Molaire & Sorriero [1] reported charge generation layer dispersion-incorporating polyester-ionomer binders with excellent interlayer adhesion. However, the stability of those dispersions is not as good as that of the polyvinyl butyral based-dispersions. The goal of the present work is twofold:

1. To optimize both adhesion and dispersion stability by combining polyvinyl butyral binders as the dispersant and polyester-ionomer binders as the adhesion promoter.
2. To produce dispersions with instantly tunable photosensitivity.

Results and Discussion

I. Dispersion Quality and Stability Optimization

In preliminary experiments, we have established that a 75:25 polyester-ionomer/polyvinyl butyral (PVB) ratio (by weight) provides good interlayer adhesion [2]. The bulk of this work concentrated on identifying the PVB structure-property relationship and a milling condition for maximizing dispersion quality and stability.

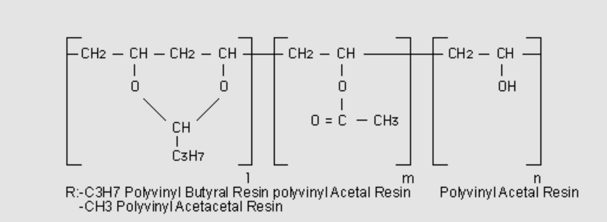

Figure 1. *Polyvinyl butyral structural formula*

The general structure of the PVB is shown in Fig. 1. Physical and chemical properties of the PVB depends upon the ratio of the elements shown in the formula. Thus, we assembled a diverse series for our experiments. Extensive experimentation has revealed that PVB B76 from Solutia behaves quite differently than PVB S-LEC BM-2 from Sesikui.

Milling Condition Optimization

Our first experiment compares these two dispersant binders against the attritor milling experiment described in Table 1.

The formulation used is described in Table 2. The experimental details are documented elsewhere [3].

Table 1: Milling conditions

Exp	Hours	RPM
1	2	200
2	2	400
3	6	200
4	6	400

Table 2: CGL dispersion basic formulation

Mill Grind	
	Grams
Pigment	23.7
PVB Dispersant	5.9
Solvent	370
Milling Media	700CC
Rinse Solvent	200

Letdown	
	Grams
Adhesive Binder	17.8
Solvent	1000
Final % Solid	3%

The behavior of particles in dispersion is described by the Herschel-Buckley equation:

$$\tau = \tau_0 + m\gamma^{p-1} \quad (1)$$

where τ is the shear stress, γ is the shear rate, m is a constant obtained by fitting, and P is the power law index. τ_0 is the yield stress that is usually present when the particles are flocculated to form a network structure. In the absence of any yield stress, the equation becomes:

$$\tau = m\gamma^{p-1} \quad (2)$$

For coating solutions where the solids concentration is less than 5%, if the ratio of the low-shear viscosity (0.5 s^{-1}) and the high-shear viscosity (3000 s^{-1}) is greater than 3.0, it is indicative of a flocculated system, and ultrasonic treatment will degrade the solution.

Table 3 reports the results of the B-76/BM-2 PVB experiment. The BM-2 dispersions are stable and insensitive to ultrasonic treatment for all but the first condition (short milling time and low RPM). On the other end, all four B-76 dispersions are ultrasonic-sensitive. An extra B-76 experiment was run, extending the milling time to 24 h at the higher RPM. That dispersion was both non-flocculated and ultrasonic-insensitive.

Table 3: Stability of B-76 and BM-2 dispersions

Example	PVB	Milling Time	Milling Speed	Viscosity. Ratio Fresh	Viscosity Ratio Sonicated
3	B-76	2	200	10.78	33.79
2	B-76	2	400	5.86	26.56
4	B-76	6	200	9.85	24.61
1	B-76	6	400	1.64	12.55
5	B-76	24	400	0.88	0.52
9	BM-2	2	200	0.97	7.72
7	BM-2	2	400	0.85	2.54
8	BM-2	6	200	1.28	1.26
6	BM-2	6	400	0.46	0.64

Table 4: PVB structure-properties experiment

PVB	% Alcohol	% Butyral	% Acetate	MW
B-72	18.9	80	1.1	170
BL-1	14.7	82.9	2.4	10
BM-1	13.6	84	2.4	60
BM-5	13.6	84	2.4	140
BM-2	12.1	85.6	2.3	100
BH-6	11.6	86.1	2.3	40
B-76	12	88	0	90
BM-S	8.4	89.4	2.2	80
BL-S	7.6	89.6	2.8	10
BL-5	7.6	90.2	2.2	30

PVB Structure-Properties Experiment

The conditions of example 9 (Table 3) were chosen as optimum for producing a stable, non-flocculated, ultrasonic-insensitive dispersion. Ten different PVB binder dispersants were carefully chosen with broad structural and molecular weight characteristics. The results of that experiment are shown in Table 5.

Table 5: PVB dispersant experiment: 4 h @ 600 RPM

Binder	Alcohol%	Butyral %	Acetate %	MW	Binder	untreated	sonicated	sonicated
B-72	18.9	80.0	1.1	170	B72	6.06	1.37	Dispersed
BL-1	14.7	82.9	2.4	10	BL1	1.41	1.01	Dispersed
BM-5	13.6	84.0	2.4	140	BM5	2.10	0.63	Dispersed
BM-1	13.6	84.0	2.4	60	BM1	1.18	2.25	Dispersed
BM-2	12.1	85.6	2.3	100	BM2	0.64	0.64	Dispersed
BH-6	11.6	86.1	2.3	40	BH-6	2.77	0.71	Dispersed
B-76	12.0	88.0	0	90	B76	1.64	12.55	Flocculated
BM-S	8.4	89.4	2.2	80	BMS	19.40	56.60	Flocculated
BL-S	7.6	89.6	2.8	10	BL-S	33.54	85.74	Flocculated

These dispersions were coated for microscopy evaluation and characterized for viscosity stability. All but three of them were stable and ultrasonic-insensitive. The B-76, BM-S, and BL-S binder dispersants that showed severe flocculation have a butyral content above 86%.

Solvent Effect Experiment

The BM-2 and the BL-S binder dispersants were chosen to evaluate solvent effects under optimized milling conditions (Table 6). The results below show no difference in performance for the four solvents. BM-2 dispersions (85.5% butyral content) are stable and ultrasonic-insensitive. BL-S dispersions (89.5 butyral content) flocculate and degrade under ultrasonic exposure.

Image Quality Evaluation

Two dispersions incorporating the BM-2 and B-76 binder dispersants, respectively, were coated as dual-layer photoconductor drums. A layer thickness series was coated for each dispersion, and image quality was evaluated on a Kodak Nexpress 2100 digital production color press. In particular, the effect of CGL optical density on image grain was evaluated. The results are reported in Tables 7 and 8, respectively, for the B-76 and BM-2 dispersions. The B-76 dispersion shows very poor image grain at the lower densities. When the dispersion was treated with ultrasonic energy, the optical density dropped sharply. The data in Table 8 show no effect of CGL thickness and density on image grain for the BM-2 dispersion.

Table 6: Solvent experiment

Example	PVB	Solvent	Visc. Ratio untreated	Visc. Ratio sonicated	Coating appearance sonicated
20	BM2 (85.6%)	**Dioxolane**	7.85	0.81	Dispersed
21	BM2	**1,1,2 TCE**	2.17	1.27	Dispersed
23	BM2	**Cyclohexanone**	0.92	1.33	Dispersed
22	BM2	**THF**	6.36	1.48	Dispersed
27	BL-S (89.6%)	**Cyclohexanone**	4.2	12.24	Flocculated
26	BL-S	**THF**	40.5	78.5	Flocculated
25	BL-S	**1,1,2 TCE**	33.5	85.7	Flocculated
24	BL-S	**Dioxolane**	25	110	Flocculated

In summary, we have established the milling conditions and the PVB structural requirements to produce charge generation dispersions that are near Newtonian, non-flocculating, and ultrasonic-insensitive. These dispersions can be prepared in a variety of solvents to produce photoconductors capable of high image quality.

Table 7: Image grain for B-76 dispersion

Ctg Speed	Before Sonication	
mm/s	CGL OD	Grain @ 0.7
1	**0.63**	**18**
1.4	**0.82**	**14**
1.8	**0.97**	**14**
	1.5 hrs After Sonication	
1	**0.71**	**14**
1.2	**0.79**	**16**
1.6	**0.96**	**14**

Table 8: Image grain for BM-2 dispersion

Ctg Speed mm/s	780nm CGL OD	Grain @ 0.7
0.8	**0.33**	**35**
1.2	**0.65**	**34**
1.4	**0.71**	**32**
1.6	**0.99**	**18**
	1hr. After Sonication	
1.6	**0.46**	**-**

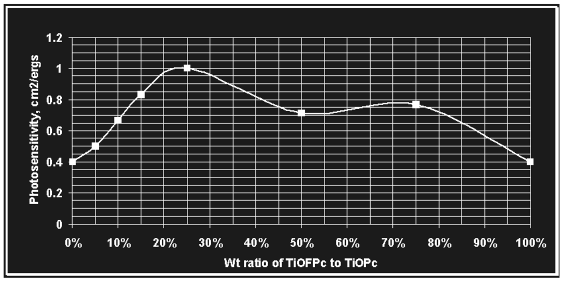

Figure 2. *Mixtures of TIOPc and TIOFPc co-crystal*

II. Instantly Tunable Photosensitivity

Our second goal was to provide charge generation dispersions that could be instantly adjusted for system-required sensitivity. We have previously reported [4-6] on our TiOPc/TiOFPc co-crystalline pigment materials with adjustable photosensitivity. During the pigment manufacturing step, the co-crystal photosensitivity is adjusted by varying the composition of the mixture from zero to 25% TiOFPc (Fig. 2). However once a composition is prepared, the photosensitivity of the final dispersion is fixed.

The photosensitivity, S, of a dual-layer photoconductor is a function of three basic factors: the photogeneration efficiency η_{gen}, the injection efficiency η_{inj}, and the transport μ. The product $\eta_{gen} \text{ x } \eta_{inj}$ is the supply efficiency that depends totally on the charge generation layer. Assuming constant transport and injection efficiency factors, one should be able to methodically control the photoconductor sensitivity by controlling the quantum efficiency of the charge generation. We have measured the quantum efficiency for TiOPc, TiOFPc, and the TiOPc/TiOFPc 75/25 co-crystal. In Fig. 3, we fit that data to the TiOFPc concentration.

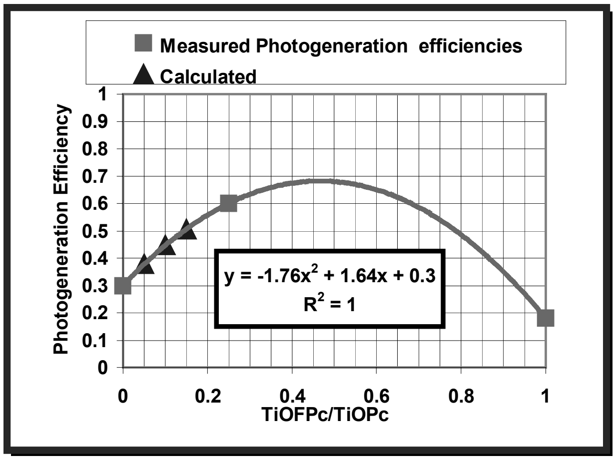

Figure 3. *Data fit to TIOFPc concentration*

Thus, the fitting equation is:

$$\eta_{gen\text{-}co\text{-}crystal} = -1.76* x^2 + 1.64*x + \eta_{gen\text{-}TiOPc} \qquad (4)$$

where x is the TiOFPc weight fraction in the co-crystal.

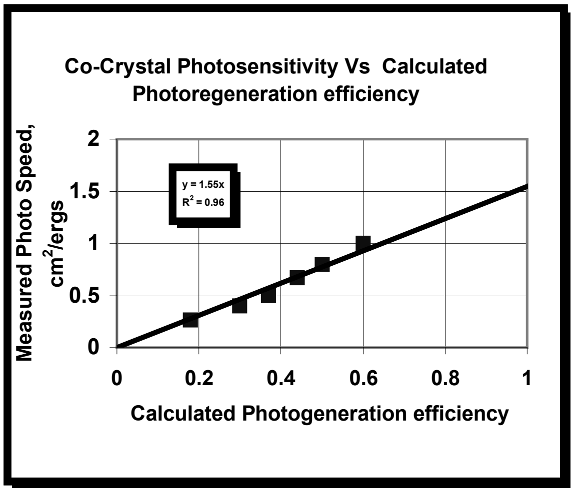

Figure 4. *Photosensitivity vs calculated photogeneration efficiencies*

Using Eq. (3), we can calculate photogeneration efficiencies for the co-crystals at 95/5, 90/10, and 85/15 of Fig. 2. The results are plotted in Fig. 4. Now we can plot the measured photosensitivity vs photogeneration efficiency, Fig. 4.

This information can be applied to design our instantly tunable charge generation dispersion. The basic concept is to use two separate dispersions, one utilizing the pure TiOFPc pigment with a low η_{gen} of 0.18, and the other the TiOPc/TiOFPc 75/25 co-crystal with a η_{gen} of 0.60. The two dispersions are made using common binders, solvent, and milling procedures and are stable, near Newtonian, and ultrasonic-insensitive. Assuming additivity and proportionality of photogeneration efficiencies, any value between 0.18 and 0.60 can be accessed by simply mixing the two dispersions in the right ratio. Thus:

$$\eta_{gen\text{-}dispersion\ Mixture} = (\eta_{gen\text{-}TiOFPc\ dispersion})* x + (\eta_{gen\text{-}co\text{-}crystal\ dispersion})* (1\text{-}x) \qquad (3)$$

where x is the weight fraction of TiOFPc dispersion in the mixture.

The data in Fig. 5 confirms this concept. We were able to fabricate photoconductors with any photosensitivity between that of our “low-speed” TiOFPc and that of our “high-speed” TiOPc/TiOFPc 75/25 co-crystal.

We can extend the range down to 0.05 cm^2/ergs by using the less sensitive form of TiOFPC as the “slow pigment” [7].

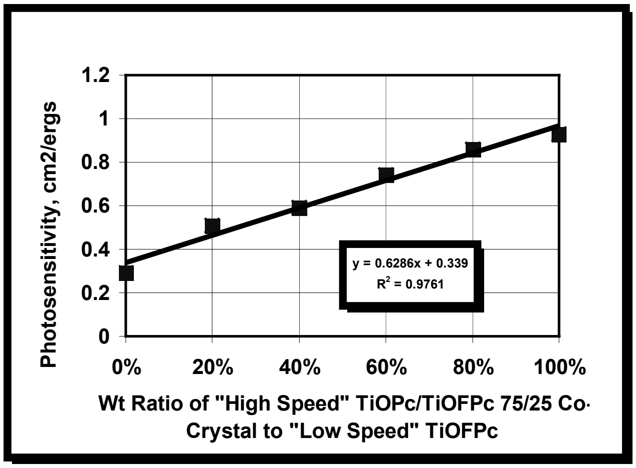

Figure 5. *Tunable charge generation mixtures system*

Conclusion

We have developed charge generation dispersions that are stable, Newtonian, ultrasonic-insensitive, and instantly photosensitivity tunable.

These dispersions are suitable for very demanding digital printing applications. Along the way, we have developed an understanding of the importance of choosing the right PVB dispersant binder.

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Reference

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Author Biography

Michel (Mike) Frantz Molaire is currently a senior research associate scientist at Eastman Kodak Company. He received his BS in chemistry, MS in chemical engineering, and MBA from the University of Rochester. His research experience includes polymer synthesis, photopolymerization, organic monomeric glasses, optical recording materials, photoelectrophotographic masters, organic photoconductor formulation, infrared sensitive pigments, and dip-coating technology. Mr. Molaire is the recipient of 43 U.S. patents, more than 75 foreign patents, and he is the author of several scientific publications. In 1984, he received the Eastman Kodak Company Research Laboratories C.E.K. Mees Award for excellence in scientific research and reporting. In 1994, he was inducted into the Eastman Kodak Company Distinguished Inventor's Gallery (Inventor Hall of Fame) for reaching the milestone of 20 or more patents. He is a member of the American Chemical Society, the Federation of Societies for Coatings Technology, and the Society for Imaging Science & Technology. He is presently VP of Programs for the IS&T Rochester local chapter.