

# Use of Sterically Stabilized Polymer Colloids as Electrostatically-Based Liquid Developers

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## Synopsis

Liquid immersion development (LID) of a latent electrostatic image has become established as an important alternative to dry toning during the past decade. In this development method, a charged, colloiddally stable colored particle that is dispersed in a dielectric fluid undergoes electrophoresis under the influence of an applied field. These particles then neutralize a latent electrostatic image of opposite polarity, which resides on either a photoreceptor drum or on dielectric paper. This results in a hard copy of the latent image being obtained. In this paper we outline the physicochemical properties that are demanded of a liquid toner and describe an alternative approach to the preparation of a LID materials package. This new approach utilizes a nonaqueous polymer colloid as the vehicle, which when colored and charged, gives a LID toner. The advantage of nonaqueous dispersions is that the steric stabilizer is irreversibly attached to the particle. Since desorption of the stabilizer is not a problem, these materials are colloiddally stable for an indefinite period of time. The particles were colored using both dyes and pigments. While neither approach was entirely satisfactory, the feasibility of coloring such particles was demonstrated. A positive charge was imparted to the particles by specific adsorption of the cation of a metal soap at the polymer-fluid interface. It was found that these experimental LID toners were able to develop a latent electrostatic image in a commercially available printer with the image being well fixed to the paper. While this approach has not been optimized, it appears to be an attractive route for preparing novel LID developers.

## INTRODUCTION

Liquid immersion development (LID) of electrostatic images on a photoreceptor drum, or on dielectric paper, has recently become an important alternative to dry toning. The reasons for the resurgence of interest in liquid development for photocopiers and printers can be attributed to the simplicity of the subsystem that can be used and also to the development of LID transfer machines which use plain paper instead of having to rely on specialty papers.

In numerous commercially available low-volume copiers a latent electrostatic image is created on a photoreceptor drum. This latent image is then toned and the image transferred to plain paper. In electronic printing, an electrostatic image is applied to dielectric paper by means of metal styli and the latent image then toned using a LID developer. The majority of LID developers<sup>1</sup> consist of a dispersion of pigment particles that are colloiddally stable, charged, and dispersed in a low viscosity insulating fluid. Upon the application of an electric field in the developer subsystem, the particles migrate and neutralize the latent image to give a hard copy print-

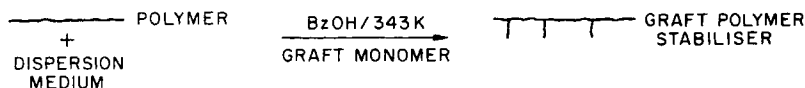
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out. All of the commercial LID copiers and printers give a black image on white paper. In this paper we describe the development of both black and of cyan-, yellow, and magenta-colored LID toners that are based on nonaqueous dispersion technology. In the first section, the use of nonaqueous dispersions as LID toners is discussed. The second section details the method of preparation and characterization of the toners while the third section discusses their physicochemical and imaging performance characteristics. It is concluded that this technology holds great promise for the preparation of a LID toner with well-defined properties and reproducible performance characteristics.

## NONAQUEOUS DISPERSIONS AND THEIR USE AS LID TONERS

The use of nonaqueous dispersions as LID developers has been described in patents issued to Hunt Chemical Corporation<sup>2,3</sup> and to Ricoh.<sup>4</sup> Nonaqueous dispersions can be defined<sup>5</sup> as submicron-size polymer particles that are dispersed in a nonaqueous medium. For LID developers the dispersion fluid is usually an odourless aliphatic hydrocarbon, e.g., Isopar G. The particles are kept as discrete colloidal entities by means of a second polymer—known as a steric stabilizer—which is soluble in the fluid dispersion medium but is irreversibly incorporated into the insoluble core particle. These particles can be polymerized in a two-stage reaction as is shown schematically in Figure 1. The first stage involves the preparation of an amphipathic block or graft copolymer which will become the steric stabilizer for the particle. This amphipathic polymer consists of two moieties: one of which is extremely soluble in the dispersion medium while the other moiety would by itself be insoluble in the dispersion medium. The second stage of this reaction consists of polymerizing the core polymer in the presence of this copolymer. The only condition that is placed on the dispersion polymerization<sup>5</sup> is that the monomer which will form the core particle should be soluble in the dispersion medium, but its polymer should be insoluble. Therefore, after initiation of the polymerization the monomer grows to a specific chain length after which it phase-separates and forms the nucleus of the core particle. The amphipathic copolymer in solution is then adsorbed onto this

### 1. AMPHIPATHIC STABILISER



### 2. DISPERSION POLYMERISATION

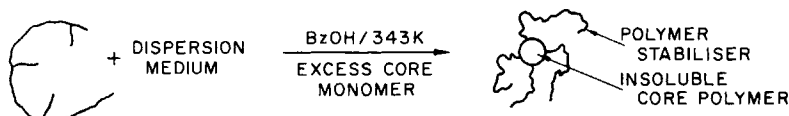


Fig. 1. Schematic of the two-stage process for preparing sterically stabilized nonaqueous latexes.

nucleus which then grows as a discrete particle. If the amphipathic polymer were not in solution, this would be a straightforward precipitation polymerization. After the reaction is complete, a milky white latex of particle size between 0.1 and 1.0  $\mu\text{m}$  diameter is obtained. A transmission electron micrograph of such a dispersion is shown in Figure 2. One of the advantages of these sterically stabilized particles is that they are indefinitely colloidally stable, unlike stabilized pigment particles that are thermodynamically metastable.<sup>6</sup> This subject will be treated in detail in the discussion section. If correctly chosen, the stabilizing moiety can also anchor the particle to the paper upon imaging. This stabilizing polymer should, therefore, ideally be a film-forming material.

In order to turn this particle into a LID toner, the particle has first to be colored. This can be carried out<sup>2-4</sup> by either ball-milling colored pigments into the particle or by dyeing the particle. We have used both techniques with varying success. The disadvantage of ball-milling in a pigment is that it is an inefficient process and unattached particles are left in the dispersion medium. If they are not removed they can cause problems during development. Dyes have the potential advantage of being easier to handle with a broad range of colors being available. All the dyes used in this study were incorporated by thermal imbibition in the dispersion medium. The disadvantage of this technique is that dye which is not taken up by the particle is dissolved in the dispersion medium and can give rise to an unwanted background image. The coloring of these particles is described in more detail in the experimental section.

Finally, the particles need to be positively or negatively charged. Within the development subsystem these particles can then undergo electrophoresis in the applied electric field to neutralize the latent image on either the photoreceptor or on paper. Numerous postulates as to the mechanism of charging nonaqueous colloids exist and these have been discussed else-

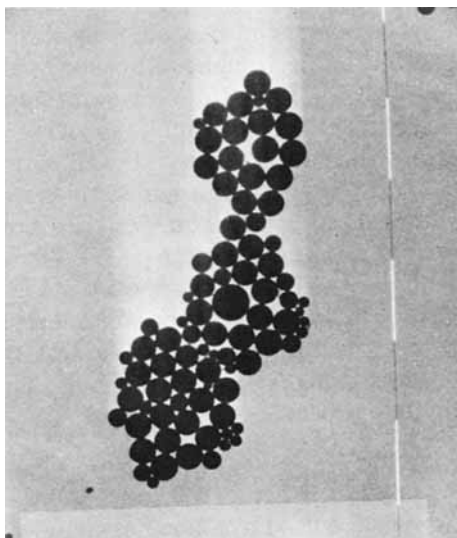


Fig. 2. Transmission electron micrograph of poly(vinyl acetate) particles. The bar corresponds to 5  $\mu\text{m}$ .

where.<sup>7</sup> The charging technique we use, because it is reproducible, is to add a material to the dispersion that ionizes in the fluid medium with one species of ion being preferentially adsorbed onto the particle surface. Ideally, the number of excess free ions in solution should be minimized since they can discharge the latent image. The factors controlling the ionization process in dielectric media are not well understood; therefore, no clear rules regarding a choice for the charge control agent can be forwarded.

## EXPERIMENTAL

### Preparation of Nonaqueous Dispersion

This is carried out in two steps as shown schematically in Figure 1. Since the dispersion medium used is Isopar G (Exxon) which is an aliphatic hydrocarbon, the polymer to be used as the steric stabilizer must be soluble in this medium. Numerous polymers have been used for this purpose and include<sup>2-4</sup> polydimethylsiloxane, polyisobutylene, poly(12-hydroxystearic acid), and poly(2-ethylhexyl methacrylate). However, in order to be effective during the dispersion polymerization, the soluble backbone has to be grafted with a polymer which by itself would be insoluble in Isopar G. One of the monomers we have found to be useful for grafting is vinyl acetate. Vinyl acetate is soluble in Isopar G, but the corresponding polymer is insoluble. This is the condition necessary for successful dispersion polymerization.<sup>5</sup> We have, therefore, used vinyl acetate in the second step of the polymerization to give a core particle of poly(vinyl acetate). Poly(2-ethylhexyl methacrylate) has been found to be a useful polymer for stabilizing particles in nonaqueous media. The results reported in this paper are for materials stabilized by this polymer. We therefore discuss the detailed preparation of poly(vinyl acetate) particles stabilized using poly(2-ethylhexyl methacrylate).

The poly(2-ethylhexyl methacrylate) used was obtained from Aldrich Chemical Co. as a 20% solution in toluene. GPC analysis indicated that  $M_w = 71,600$  with  $M_w/M_n = 5.54$ . The toluene was removed, using a rotary evaporator before use. Poly(2-ethyl hexyl methacrylate) (40 g) was dissolved in Isopar G (300 mL) and the solution purged with nitrogen for 30 min at 353 K; benzoyl peroxide (0.3 g) was then added to the solution. After 2 h the temperature was lowered to 343 K, and vinyl acetate (4 mL) was added to this mixture. Grafting was then allowed to proceed for  $\sim 18$  h, after which more vinyl acetate (160 mL) and benzoyl peroxide (0.8 g) were added simultaneously to the graft copolymer mixture. Polymerization was allowed to proceed for a further 20 h. Residual monomer was then removed from the reaction mixture, and the dispersion then cooled. The solids content of the dispersion was ca. 40% w/v.

### Preparation of LID Toners

Both dyes and pigments were used to color the particles. The hydrocarbon soluble dyes that were used were Sudan Black B (CI 26150, Fisher Scientific) and Sudan Red 7B (CI 26050, Aldrich). The pigments used were Toner 8200

(Paul Uhlich), Eastman Polyester Yellow (Eastman), DuPont Latyl Brilliant Blue (DuPont), and Amasolve Cervise P (American Cyanamid). The last three pigments are colored yellow, cyan, and magenta, respectively.

There are a large number of chemicals to be found in the patent literature that are claimed to be useful as charge control agents for colloidal particles in nonaqueous media.<sup>7</sup> In this series of experiments, zirconium octoate (Nuodex) was used to impart a positive charge to the latex particles. It was obtained as a 6% w/v solution in mineral spirits and was used as received.

The Sudan Black B dye was used without purification by dissolving 0.5 g of dye in 30 mL of Isopar G. However, the Sudan Red 7B dye was obtained from the manufacturer in the form of coarse particles that were sparingly soluble in Isopar G at ambient temperatures. Therefore, this dye was heated at 353 K in Isopar G in order to dissolve the dye and the solution filtered through glass wool before use. The latex was diluted to ca. 20% w/v of particles and to 30 mL of this dispersion was added 30 mL of the dyed Isopar G. The dispersion was then stirred gently at 353 K for ca. 2 h to give a dyed latex. After cooling, 20 mL of the dyed dispersion was mixed with 10 mL of zirconium octoate. This mixture was diluted with 1 L of Isopar G to give a working ink containing ca. 0.2% w/v of particulate matter.

In order to color the latices using pigments, 0.8 g of the pigment was attrited (Union Process Model 01) in Isopar G for 20 h in order to grind the pigment to submicron size. 80 mL of a 10% w/v sample of latex was added to the pigment dispersion, and the mixture attrited slowly for 1 h. Twenty-five mL of this dispersion was then diluted in 1 L of Isopar G and 5 mL of zirconium octoate added as the charge control agent to make the working ink. A second 25-mL portion of the cyan, magenta and yellow toner concentrates were heated at 90°C for 30 min before being diluted and charged to make the working ink. This was carried out in order to molecularly dissolve the pigment in the core of the polymer particle thereby amplifying the color characteristics of the developer.

### Characterization of the Toners

The characteristics of toners which are of primary importance are the particle size, colloidal stability of the ink, its charge/mass, i.e.,  $Q/M$  ratio, its color characteristics, and its imaging performance.

**Particle Size.** The particle size of the latex and also of the working ink were measured *in situ* using a Coulter Nanosizer which is a simple fixed-angle correlation spectrometer. Some of the samples were also cast onto a carbon grid and analyzed using transmission electron microscopy (Philips EM400).

**Colloid Stability.** These developers should remain as discrete particles over the lifetime of the toner and should possess good freeze-thaw characteristics. The colloidal stability was monitored by measuring the particle size over a period of several months after being allowed to undergo gravitational setting.

**Electrical Characterization.** In LID technology the developers are usually characterized by their charge/mass ratio since this can be readily measured and provides a useful criteria for machine performance. It is a

measure of the electrokinetic parameters of the colloidal developer. This will be considered in detail in the discussion section. We have adopted the method of measuring  $Q/M$  published by Novotny and Hair,<sup>8</sup> which is based on an analysis of the current-time characteristics of the dispersion and has been described in detail elsewhere.<sup>7</sup>

**Color Characteristics and Imaging Performance.** This was carried out by placing the experimental toner in a Versatec 1200 printer/plotter and printing a variety of preselected test patterns. Solid area images were sputter-coated with a 200 Å layer of a gold/palladium alloy and viewed in a scanning electron microscope (Philips SEM 505). The optical density of the solid area image in reflection was measured using a Tobias Associates Densitometer (Model RCX) using the appropriate filters while the color characteristics were measured using an IBM 7409 Scanning Color Sensor and analyzed using the IBM 7410 Color Analyzer. Illuminant C was used with the standard 2° observation angle. All measurements were made in the reflectance mode and calibrated against a white standard. Both the spectral response of the solid area images and the CIELAB color coordinates<sup>9</sup> are reported.

## RESULTS AND DISCUSSION

The important properties that affect the performance of the toner are: (i) the stability of the colloidal dispersion; (ii) its electrical characteristics, i.e.,  $Q/M$ ; and (iii) its color characteristics and imaging performance, which includes its adhesion to paper. These subjects are discussed individually since they allow some insights into the parameters that have to be taken into consideration in formulating a LID materials package.

### Colloid Stability

The colloidal particles constituting the developer should remain as discrete entities over the lifetime of the toner. This is not an insignificant problem since by definition colloidal dispersions are almost always thermodynamically metastable.<sup>6</sup> If naked colloidal particles are dispersed in a fluid medium, they coagulate quickly due to the attractive van der Waals forces ( $V_A$ ) that exist between the particles. In order to stabilize the dispersion, a repulsive potential ( $V_R$ ) must be introduced between the particles such that  $V_R > V_A$ . This can be achieved either by introducing a steric barrier or by introducing a repulsive electrostatic potential between the particles. Since in LID development the particle charge gives rise to its transport properties and the  $Q/M$  ratio of the toner will depend upon the application for which it is to be used,<sup>10</sup> the charging and stabilization functions in the toner should be separated. Therefore, we choose to stabilize the particles by a steric stabilization mechanism and the charge enables the particles to undergo electrophoresis in the development subsystem.

One of the problems with a steric stabilizer is that desorption of the stabilizer can occur allowing the attractive forces to coagulate the particles. A prime reason for utilizing a nonaqueous dispersion as the LID particle is that the polymeric stabilizer is terminally attached to the particle surface

so that desorption is not a problem. The total particle interaction  $V$  of two particles in a dispersion is given by

$$V = V_A + V_R \quad (1)$$

where  $V_R$  is now the repulsive interaction induced by the steric stabilizer. The van der Waals attraction can be written<sup>11</sup> as

$$V_A = -\frac{Aa}{12H} \quad (2)$$

where  $A$  is the Hamaker constant and  $H = R - 2a$ , where  $R$  is the center-to-center distance between particles of radius  $a$ . The Hamaker constants for polymers are in general an order of magnitude smaller<sup>6,12</sup> than those for inorganic pigments which makes van der Waals forces between such particles extremely weak. Nonaqueous dispersions are, therefore, readily stabilized even by fairly short steric stabilizing chains, as has been discussed in more detail elsewhere.<sup>10</sup> Numerous expressions for  $V_R$  can be found in the literature,<sup>6,13-15</sup> most of which are based on the dilute solution theory of Flory and Krigbaum.<sup>16</sup> The repulsive steric potential caused by the interpenetration of the stabilizing chains of adjacent particles is of the form<sup>6,13-15</sup>

$$V_R = B\left(\frac{1}{2} - \chi\right) aSkT \quad (3)$$

where  $B$  is a function of the molecular parameters of the steric stabilizer and the dispersion medium and is always a positive quantity,  $S$  is a function that accounts for the distance dependence of the particle interaction, and  $\chi$  is a parameter which is a measure of the antipathy between the stabilizing polymer and the dispersion medium. Equation (3) predicts that the dispersion will be stable when  $V_R$  is positive, which means that  $\chi < 0.5$ . When  $\chi > 0.5$ ,  $V_R$  is negative and the system flocculates. The condition  $\chi = 0.5$  corresponds to the theta ( $\theta$ ) point of a polymer solution.<sup>17</sup> Therefore, the  $\theta$  point for the sterically stabilizing polymer in the dispersion media represents the limit of stability of the nonaqueous dispersion.<sup>6</sup> However, for nonpolar polymer solutions there are, in principle, two  $\theta$  temperatures<sup>18</sup> as is shown schematically in Figure 3(a). These are known as the  $\theta$  temperature associated with the upper critical solution temperature,  $\theta_U$ , and that associated with the lower critical solution temperature,  $\theta_L$ . Between  $\theta_U$  and  $\theta_L$  the solution is homogeneous but for  $T > \theta_L$  and  $T < \theta_U$  the solution is phase-separated. Similarly, the nonaqueous dispersion stabilized by poly(2-ethylhexyl methacrylate) dispersed in Isopar G will be stable between  $\theta_U$  and  $\theta_L$  but will be flocculated outside that temperature range. At the two  $\theta$  temperatures,  $\chi = 0.5$ , but between these two temperatures,  $\chi < 0.5$  and

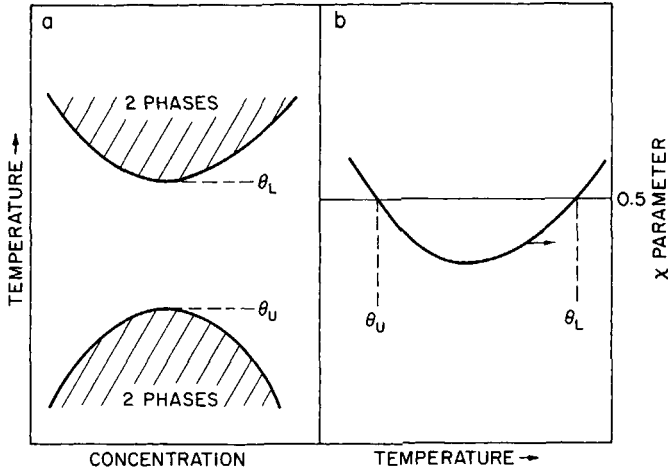


Fig. 3. (a) Schematic diagram of a hypothetical infinite molecular weight polymer which shows phase separation occurring at the  $\theta$  temperature associated with the UCST and the  $\theta$  temperature associated with the LCST; (b) shows schematically the variation in the  $\chi$  parameter between  $\theta_L$  and  $\theta_U$ .

varies monotonically with the temperature as is indicated in Figure 3(b). A detailed theoretical interpretation of this behavior has been given elsewhere.<sup>13</sup> It suffices to say that when a temperature dependent  $\chi$  is put in eq. (3),  $V_R$  varies as a function of temperature as is shown in Figure 4. Unfortunately, no thermodynamic data exists for poly(2-ethylhexyl methacrylate) in Isopar G which precludes any quantitative calculations for this system. It is possible, though, to obtain an estimate of the critical flocculation temperatures associated with the two theta temperatures. The  $\theta_L$  of a polymer solution is of the order of  $0.8 T_c$ , where  $T_c$  is the critical temperature of the solvent.<sup>19</sup> If we assume that Isopar G is analagous to *n*-dodecane, then the upper critical flocculation temperature of the poly(vinyl acetate) dispersion would be in excess of 500 K. We have found experimentally that these dispersions are stable up to at least 350 K. Unfortun-

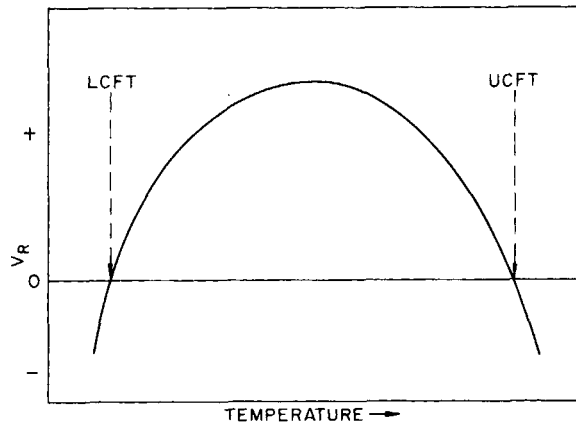


Fig. 4. Schematic diagram of the variation in  $V_R$  between the upper and lower critical flocculation temperatures for one distance of close approach of the particles.



nately, there are no empirical rules for predicting  $\theta_U$  of a polymer solution. Experimentally we have found that a solution of poly(2-ethylhexyl methacrylate) in Isopar G becomes glassy when immersed in a dry ice-acetone mixture. However, no indication of phase separation at these temperatures was noted; therefore, the lower critical flocculation temperature of the system appears to be lower than 200 K. The practical stability range for a commercial developer should be from ca. 270 to 320 K, and these latices and dyed latices more than meet this requirement. This is not true for all of the pigmented latices as will be discussed later.

A crucial stability test is whether the toner remains as discrete particles after being left to settle undisturbed for periods of up to a year, i.e., the normal shelf life of a developer. This is carried out by measuring the particle size of the toner after it has been allowed to remain undisturbed for periods of up to 12 months. We have observed that the latices without colorant are extremely stable with a particle diameter of 0.1–0.5  $\mu\text{m}$ , which does not vary with time. When the lattices have been dyed the particle size distribution of the toner increases to 0.1–1.0  $\mu\text{m}$ . This is caused by some of the dye crystallizing in the Isopar G and the latices attaching themselves to these needlelike crystals as is shown in Figure 5(a). However, these working toners were easily redispersed after being left to settle for numerous months thereby exhibiting an acceptable colloidal stability.

The ball-milling of pigments into the latices also increased the particle size of the developer. For example, the Toner 8200 increased the particle size with particles in excess of ca. 2  $\mu\text{m}$  diameter being observed. The composite particles formed using this technique are shown in Figure 5(b). The electron micrograph shows numerous latex particles surrounding a

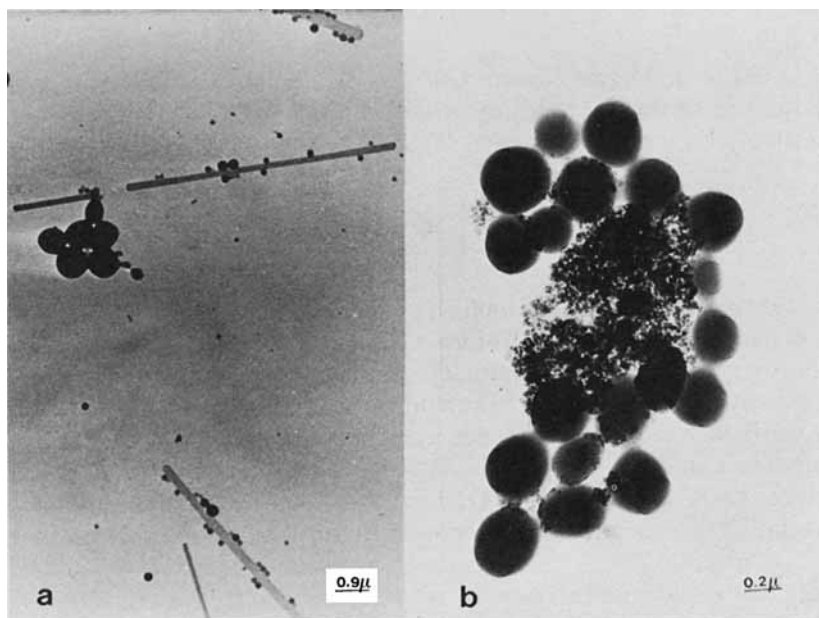


Fig. 5. (a) Transmission electron micrograph of poly(vinyl acetate) latexes surrounding a crystal of Victoria Blue; (b) transmission electron micrograph of poly(vinyl acetate) latexes after ball milling with Toner 8200.

carbon black particle. These inks were found to settle and coagulate extremely quickly, making them unacceptable as LID inks. With the colored pigments the particle size distribution was found to be much narrower, i.e., 0.1–1.0  $\mu\text{m}$  diameter with good incorporation of the pigment into the particle. Although these dispersions settled, they were easily redispersed after being left undisturbed for up to 6 months and were therefore considered to exhibit an acceptable shelf-life stability.

### Electrical Characterization

The charging of particles in dielectric media is a subject which is at present not well understood.<sup>7,20</sup> In general, particles dispersed in liquids can be charged in one of three ways: (a) by contact electrification; (b) by proton transfer; (c) by selective adsorption of ions at the solid fluid interface. We have used the selective adsorption approach in these studies since it has been found to give reproducible test results. A large variety of metal soaps are mentioned in the patent literature as being able to ionize in Isopar G. We have found<sup>7</sup> numerous materials to be useful as charge control agents, although we have used zirconium octoate exclusively in this series of experiments.

In LID technology, the  $Q/M$  ratio of the toners is usually used to characterize them.<sup>8</sup> It is therefore desirable to understand the significance of this ratio from electrokinetic theory, and this has been discussed in detail in a previous publication.<sup>7</sup> Using well-known expressions for the charge ( $Q$ ) and the mass ( $M$ ), the  $Q/M$  ratio can be written as

$$\frac{Q}{M} = \frac{3\epsilon\zeta}{a^2\rho} \quad (4)$$

where  $\epsilon$  is the dielectric constant of the dispersion medium and  $\zeta$  is the zeta potential of the particles of density  $\rho$  and radius  $a$ . Equation (4) can alternatively be written as<sup>7</sup>

$$\frac{Q}{M} = \frac{3\eta u}{2a^2\rho} \quad (5)$$

where  $u$  is the electrophoretic mobility of the particles and  $\eta$  is the viscosity of the dispersion medium. Therefore,  $Q/M$  is proportional to  $u/a^2$ , the electrophoretic mobility of the system. Qualitatively, we can say that for rapid development of the image,  $Q/M$  should be large. However, the optical density of the developed image depends upon the number of particles deposited per unit area, and this will obviously be dependent upon the  $Q/M$  value. Therefore, there is obviously a trade-off between development speed and optical density. This should be borne in mind in designing a commercial toner.

When the experimental inks were tested without the addition of the charge agent, it was observed that most of the dispersions possessed a slight positive charge. The  $Q/M$  values for these systems could not be determined with any degree of accuracy, but they would usually possess a  $Q/M$  ratio

less than ca.  $25 \mu\text{C g}^{-1}$ . Upon the addition of zirconium octoate all the particles become positively charged and the  $Q/M$  ratio could be varied in the range  $100\text{--}1200 \mu\text{C} \cdot \text{g}^{-1}$ , depending upon the amount of charge control agent added to the dispersion. Measurement of  $Q/M$  as a function of the amount of charge control agent added to the poly(vinyl acetate) lattices containing Eastman Polyester Yellow is shown in Figure 6. It can be seen that  $Q/M$  increases almost linearly until at a critical concentration of zirconium octoate  $Q/M$  becomes constant. It was found previously,<sup>7</sup> using carbon black based toners, that the concentration at which  $Q/M$  attained a constant value was very dependent upon the metal ion used. This reflects the affinity of the metal ion for the surface of the particle. A detailed study of this effect has not been carried out for these polymer latex based inks, although it is thought that the same effects will be observed. A study of this type would be necessary if the system was to be optimized for a specific application.

From eqs. (4) and (5), it is possible to extract electrokinetic data from  $Q/M$  measurements. It should be borne in mind that these measurements are of limited precision; therefore, the value of the mobilities and zeta potentials obtained should be viewed with caution. The  $Q/M$  measurements yield  $\zeta$  values which have a range of  $40\text{--}220$  mV while  $u$  values vary over the range ca.  $1\text{--}7 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ . It should be mentioned that the upper  $\zeta$  potential values reported here are much larger than those generally found in the colloid literature where values typically range from  $20$  to  $120$  mV. The reason for this discrepancy is not understood. From studies of the adsorption isotherms of metal soaps on inorganic substrates<sup>21</sup> it has been calculated that each molecule occupies ca.  $100 \text{ \AA}$  on the solid surface, and coverage usually saturates at about one monolayer. If we assume that a similar behavior is observed at organic surfaces, then it becomes clear from the apparent ionization factor that only about one molecule in  $10,000$  con-

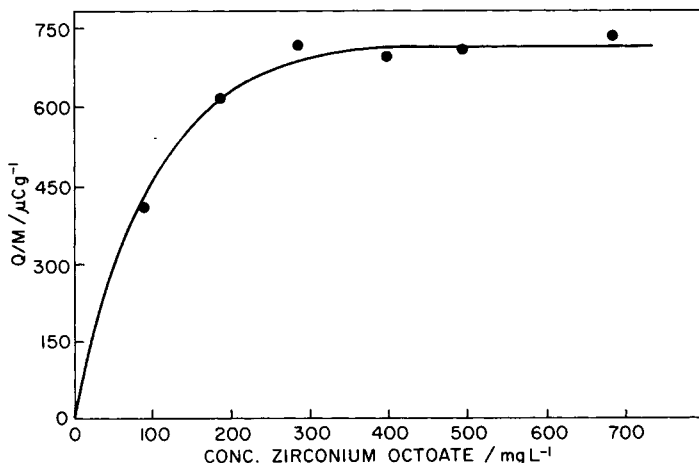


Fig. 6. The charge-to-mass ratio of the poly(vinyl acetate) latexes colored with Eastman Polyester Yellow is shown plotted as a function of the concentration of zirconium octoate added to the developer.

tributes to the particle charge. This should probably be considered a lower limit for the dissociation of these molecules at the solid-fluid interface since other contributions to this process have not been taken into account.

### Color and Imaging Performance Characteristics

The experimental toners described in this paper were all found to image in a Versatec 1200 Printer/Plotter. The optical density of each image and the CIELAB color coordinates are shown in Table I. It is apparent that the optical density of the solid area images is too low to be practically useful. This can be overcome, to some extent, by increasing the solids content in the dispersion although this introduces other problems such as acceptable fixing of the image. Table I also indicates that the pigmented toners gave denser images with less background than did the dyed toners. In fact, a major problem with the dyed materials is that the excess dye gives rise to excessive conductivity as well as image background problems. The results reported in Table I for the pigment-based developers refers only to the heat-amplified images. Without this amplification process, i.e., the pigment becomes a dye on heating in the poly(vinyl acetate) binder, the images obtained were dull and certainly did not approximate the cyan, magenta, and yellow hues anticipated. It was noted that the developer colored with Amasolve Cervise P gave a "grainy" image, which is thought to be due to the pigment particles not being molecularly dispersed in the polymer on heating. The

TABLE I  
Color Characteristics and Imaging Performance of Poly(vinyl Acetate)-Based  
Liquid Developers

Colorant	Optical density	CIELAB coordinates			Fixing properties	Comments
		$L^*$	$a^*$	$b^*$		
Toner 8200	0.8	—	—	—	Poor	Colloidally unstable, poor image quality
Eastman Polyester Yellow	0.34	86.42	-13.11	43.48	Excellent after heating	Good image quality
DuPont Latyl Brilliant Blue	0.22	83.18	-5.38	-4.88	Excellent after heating	Good image quality
Amasolve Cervise P	0.28	76.48	15.42	-11.31	Excellent after heating	Image "grainy," poor quality
Sudan Black B	0.11	—	—	—	Good	Considerable background image, color appears to fade
Sudan Red 7B	0.14	—	—	—	Good	Considerable background image, color appears to fade

images obtained from the Eastman Polyester Yellow and DuPont Latyl Brilliant Blue based toners were high resolution images. The diffuse reflectance spectral response of these images are shown in Figure 7 while the  $L^*$ ,  $a^*$ , and  $b^*$  coordinates are given in Table I. The spectral response of the Polyester Yellow indicates that it has the correct color characteristics. The image from the Amasolve Cervise P toner shows a blue response at ca. 430 nm, which is also indicated by the rather large negative  $b^*$  value. It is therefore a poor magenta color. The spectrophotometric data for the DuPont Latyl Brilliant Blue, i.e., cyan, sample and the CIELAB  $b^*$  value shows that this hue is too yellow. These materials would therefore be acceptable as functional colour toners but would probably be deficient for a pictorial color system.

The adhesion of the LID image to paper must be adequate to avoid ruboff of the image on handling. Numerous factors can contribute to the fixing characteristics such as the roughness, the properties of the paper surface and the film-forming characteristics of the steric stabilizer and polymeric core of the developer. Since little research has been reported in this area, it is difficult to assess the relative importance of the various factors entering into the fixing process. A practical, if somewhat subjective test of fixing, is to see whether the image can be removed with adhesive tape. If the optical density of the image remains unchanged by this test, then the fixing properties are adequate. With the exception of the Toner 8200 based material, all of the toners reported here showed good fixing characteristics.

### CONCLUDING REMARKS

Liquid Immersion Development is a process of toning a latent electrostatic image which utilizes the electric field migration of a charged pigment particle through a dielectric fluid dispersion medium. This concept is able to provide for a low-cost, high-resolution image on paper.

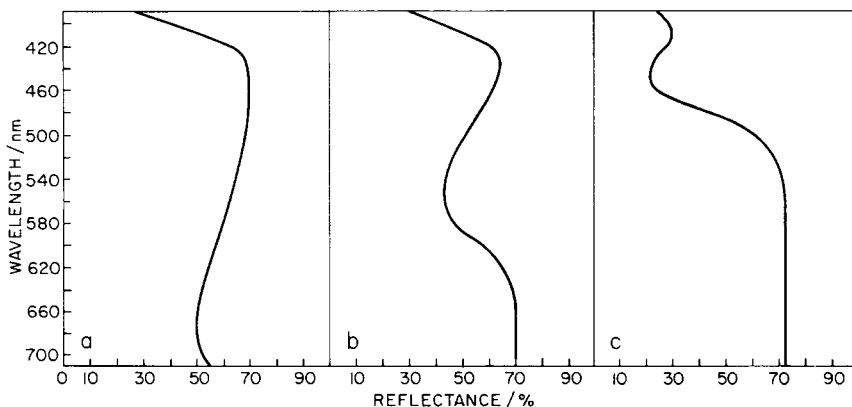


Fig. 7. The diffuse reflectance spectral response of the images obtained from the poly(vinyl acetate) latex based developers is shown: (a) refers to the toner dyed with Latyl Brilliant Blue, (b) was dyed with Amasolve Cervise P, and (c) was dyed with Eastman Polyester Yellow.

This method of toning a latent electrostatic image is conceptually extremely simple and appealing. In practice, it is necessary to prepare a dispersion of particles which have specific electrical and colloidal properties in suspension but possesses specific optical and adhesive properties when attached to a substrate.

In this article we have utilized a nonaqueous polymer colloid as the vehicle which, when colored and charged, gives a LID toner. The advantage of these nonaqueous dispersions is that the steric stabilizer is irreversibly attached to the particle. Since desorption of the stabilizer is not a problem, these materials are colloidally stable for an indefinite period of time. These particles were colored using both dyes and pigments. While neither approach was entirely satisfactory, the feasibility of coloring such particles was demonstrated. Charge was imparted to the particles by specific adsorption of the cation of a metal soap at the polymer-fluid interface. It was found that these experimental LID toners were able to develop a latent electrostatic image in a commercially available printer. The fixing of the image to paper was found to be extremely good in comparison with most commercially available developers.

There are, at present, numerous electrophotographic copiers and electrophotographic printers in the marketplace that make use of liquid toners for developing a latent electrostatic image. These toners have been made on a trial and error basis with little thought given to the underlying scientific principles involved in such systems. The purpose of this paper has been to delineate what we think are the important issues and problems with regard to liquid developers and to offer an alternative approach to preparing LID toners. While much work remains to be done to optimize the concept proposed here, only by taking such a systematic approach will an improved materials package be obtained.

### References

1. C. J. Claus and E. F. Mayer, in *Xerography and Related Processes*, Ed. J. Dessauer and H. Clark, Eds., Focal Press, New York, 1965, Chap. 22.
2. G. E. Kosel, U.S. Pat. 3,900,412, 1975.
3. G. E. Kosel, U.S. Pat. 3,990,980, 1976.
4. K. Tsubuko, T. Kurotori, T. Kimura, T. Kawanishi, and Y. Kareko, U.S. Pat. 4,081,391, 1978.
5. K. E. J. Barrett, *Dispersion Polymerization in Organic Media*, Wiley, London, 1975.
6. D. H. Napper, *J. Colloid Interface Sci.*, **58**, 390 (1977).
7. M. D. Croucher, S. Drappel, J. Duff, K. Lok, and R. W. Wong, *Colloids Surfaces*, to appear.
8. V. Novotny and M. L. Hair, *J. Colloid Interface Sci.*, **71**, 273 (1979).
9. A. R. Robertson, *Color Res. Appl.* **2**, 7 (1977).
10. M. D. Croucher, S. Drappel, J. Duff, G. Hamer, K. Lok, and R. W. Wong, *Photographic Sci. Eng.*, **28**, 119 (1984).
11. P. C. Hiemenz, in *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1977, Chap. 10.
12. J. Visser, *Adv. Colloid Interface Sci.*, **3**, 331 (1972).
13. M. D. Croucher and M. L. Hair, *J. Phys. Chem.*, **83**, 1712 (1979).
14. A. K. Dolan and S. F. Edwards, *Proc. Roy. Soc. London*, **A343**, 427 (1965).
15. R. H. Ottewill and T. Walker, *Colloid Z. Z. Polym.*, **227**, 108 (1968).
16. P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).
17. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953, Chap. 12.

18. D. Patterson, *Rubber Chem. Technol.* **40**, 1 (1967).
19. M. D. Croucher and M. L. Hair, *J. Colloid Interface Sci.*, **81**, 257 (1981).
20. F. M. Fowkes, F. W. Anderson, R. J. Moore, H. Jinnai, and M. A. Mostafa, *Am. Chem. Soc., Symp. Ser.*, **200**, 307 (1982).
21. V. Novotny, *Colloids Surfaces*, **2**, 373 (1981).

Received February 24, 1984

Accepted June 18, 1984