Designing of Liquid Toner Materials in Hydrocarbon and Perfluorinated Solvents

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Abstract

Liquid toners for Electrophotographic applications are colloidal dispersions of charged particles (0.1-0.5µ) colored by a dye or pigment in a solvent of very low dielectric constant. The stability of particle systems in such solvents is effected by soluble polymers with a positive charge either by adsorption or chemical interaction. For hydrocarbon solvents such as Isopar™ (δ~7.2), polymers and copolymers largely comprising lauryl methacrylate (LMA) and isobornyl acrylate (IBOA) with solubility parameters (δ) of 7.9 and 7.8 respectively serve as polymeric dispersants for organic pigments. Macromers of such polymers can stabilize organosols produced by dispersion polymerization. For perfluorinated solvents (Fluorinert™), perfluoroacrylate polymers or macromers serve as dispersants for all types of particles. Fine particles of perfluorinated polymers can also be generated by significantly modifying the Flory-Huggins polymer-Fluorinert™ interaction parameter χ of the said polymers to >>0.5 by insertion in the main chain or pendant position segments that are thermodynamically immiscible resulting in the collapse of the chain. Incorporation of siloxane or perfluoroalkyl units in polyacrylate dispersants facilitate the release of toner films from photoconductor surface in electrophotography.

Introduction

Liquid toner systems which are colloidal dispersions of submicron particles comprising pigment bound by a film forming resin and a charge director in a low dielectric constant solvent are highly suitable for digital printing of high resolution images and reproducible continuous tones in spite of problems of liquid handling, colloid stability and environmental concerns[1,2]. In spite of the dominance of the dry toner systems where these problems are addressed along with continuous improvement in image resolution, liquid toners present many opportunities in the development of high density electronic circuits on desired substrates, resistors and many novel application areas[3]. This work mainly deals with the development of materials that constitute the colloidal system of particles both in isoparaffinic hydrocarbon solvents such as Isopar™ and in more environmentally friendly solvents of the type Fluorinerts™ which are perfluorinated hydrocarbons or polyethers. The topics presented are a) Design of polymeric dispersants for pigments based on polymer compatibilities and film formation and charging of the toner particles and b) Strategies to generate colloidal particles in Fluorinerts.

Design of Polymeric Dispersants in Isopar™

Polymeric dispersants suitable for stabilizing a system of submicron particles in Isopar™ are required to be soluble in the solvent and carry a sufficient density of electrostatic charges. Figure 1 shows the structure of a random copolymer system designed to meet the above criteria:

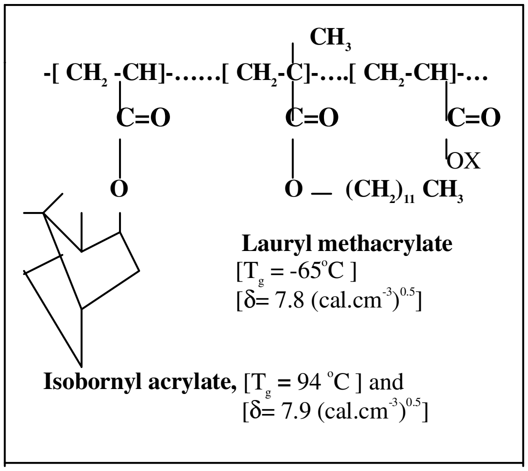


Figure 1. A Polymeric dispersant soluble in Isopar

The design of the dispersant illustrated is based on the fact that Poly(isobornyl acrylate) (PIBOA) and Poly(lauryl methacrylate) (PLMA) satisfy the condition of thermodynamic miscibility[4] as shown by :

$$[\mathbf{B\ M} / \rho\ \mathbf{RT}] < 2 \qquad (1)$$

where $\mathbf{B}=(\delta_A - \delta_B)^2$; $\mathbf{M}$= Polymer Molecular Weight; ρ = density and at the same time the polymer should have solubility in Isopar™. The solubility parameters δ_A, δ_B of PIBOA and PLMA are 7.9 and 7.8 [$(\mathrm{cal.cm}^{-3})^{0.5}$] respectively, nearly matching the value for Isopar at 7.2, thus yielding a transparent film of the polymer and hence higher optical density for the pigmented film. The solubility of the dispersant in Isopar™ was found to be maintained when the polymeric chain constituted a minimum of ~70 wt. percent of the total of PIBOA and PLMA in varying ratios, thus providing a range of Glass Transition temperatures (T_g) for the polymeric film to achieve the desired flexibility for the toner film for effective film formation during the toning of the latent image and its subsequent transfer to the desired receptor surface[5,7]. The rest of the 30% of the chain could carry a) any pendant moiety X:

X = CH_2- CH_2-O-CO CH_2-CO CH_3

(see *Figure 1*) such as an actylacetonate group for complexing cationic charging agents such as **Zr^{4+}** to provide a positive charge to the colloidal dispersion and a variety of other pendant groups to impart any desirable property to the toner film. The toner for electrographic or electrophotographic imaging is prapared by high shear media mill grinding of a suspension of the desired pigment and the soluble dispersant in ratios of 1:2 to 1:4 along with a charge director such as an isopar soluble organic salt of Zr^{4+} such as a neodecanaoate. The conductance of a toner of ~1% solids is normally in the range of 1-10 picomhos/cm. with particle sizes in the range 200-600nm. The amount of the charge director is specific to the imaging system. The toner charge determines the amount of the toner deposited on the developer, which in turn determined the optical density of the image.

Liquid toners are also prepared by dispersion polymerization of monomers such as acrylics in Isopar™. Such polymerizations are conducted in the presence of macromers – the dispersant chains such as those described in *Figure 1*carrying a polymerizable end group. The dispersion droplets of the monomers stabilized by the dispersant comonomer after polymerization yield an organosol which is a colloidal dispersion of polymeric particles in the hydrocarbon solvent. The molecular weight of the stabilizing macromers was in the range 1-5 10^5 as determined by NMR These chains from the macromer constitute the shell of the particles which imparts stabilization to the colloidal system by providing solvated chains in the solvent (entropic stabilization) besides the electrostatic stabilization provided by the charge on the particles as illustrated in *Figure 2* below:

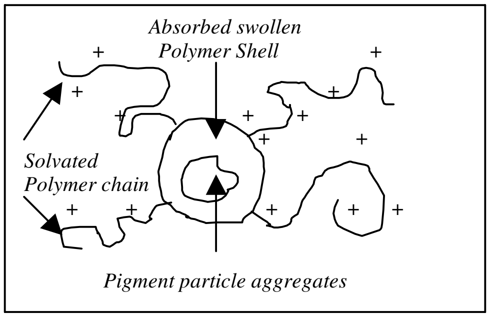


Figure 2. An illustration of a liquid toner particle

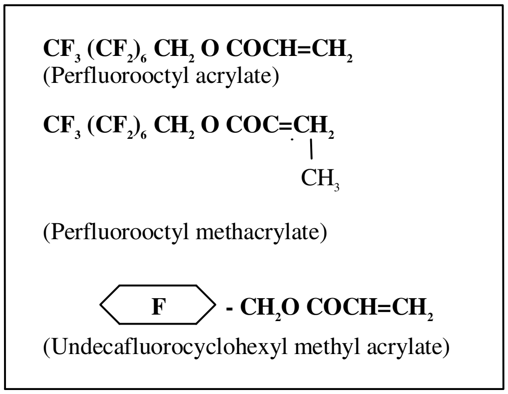
Liquid toners are made from organosols by subjecting to media mill grinding in the presence of pigments and charge directors in the same manner as described for the preparation of toners from soluble polymers. The toner particle may be visualized as a possible aggregate of the adhering latex (sol) particles to the pigment surface, with the solvated chains from the organosol particles providing entropic and electrostatic stabilization**.**

Strategies to Generate Colloidal Particles in Fluorinert™ Solvents and Preparation of Liquid Toners

Fluorinert™ solvents of boiling range 50-250 °C produced by 3M Corporation are nontoxic, inert and environmentally friendly but have negligible solubility for any nonfluorinated nomomers or polymers. Using a few fluorinated monomers and their polymers, a few strategies have been developed to prepare toners from soluble polymers or from hydrocarbon based acrylic particles. Liquid toners are prepared either from soluble polymeric dispersants or a colloidal system of particles by media mill grinding with pigments in the presence of charging agents as described before.

Polymer Particle Generation In Fluorinert™ Solvents—*Method 1*

Polymerization of a perfluorinated monomer or mixtures shown in *Figure 3* yields a solvent-soluble polymer. However, if a calculated amount of a hydrocarbon monomer is mixed with the above and the mixture is polymerized, then the incorporation of hydrocarbon units into the fluorochemical chain would produce a collapse of the polymer chain in Fluorinert™ solvent and under suitable conditions of emulsification by surfactants, a stable suspension would result. The insolubility of the perfluorinated polymer chain induced by copolymerized hydrocarbon units is the result of the Solubility Parameter difference between the latter and the Fluorinert solvent and the consequent increase of the Flory-Huggins Polymer-Solvent Interaction Parameter **χ** to >0.5. This can be shown by the Hildebrand approach to miscibility of nonpolar systems[6] , assuming the volume of a polymer repeat unit **v** ~100 cm^3/mol



$CF_3(CF_2)_6CH_2$ O COCH=CH_2
(Perfluorooctyl acrylate)

$CF_3(CF_2)_6CH_2$ O COC(CH$_3$)=CH_2

(Perfluorooctyl methacrylate)

F - CH_2O COCH=CH_2
(Undecafluorocyclohexyl methyl acrylate)

Figure 3. Monomers yielding soluble polymers in Perfluorinated solvents

$$\chi = 0.34 + v\frac{(\delta_1 - \delta_2)^2}{RT} \tag{2}$$

Assuming $[\delta_{\text{fluorinert}} - \delta_{\text{hydrocarbon}}] = 2.5$,

$$\chi = 0.34 + \frac{100\,(2.5)^2}{1.98\,(298)} = 1.4\text{-}1.7 \qquad (3)$$

Therefore $\chi >>> 0.5$ and the expansion factor of the polymer chain in solvent[7] becomes <1 and as a result, the solvated polymer chain is collapsed as illustrated in the following expression[7] relating the expansion factor α and the interaction parameter χ:

$$\alpha^5 - \alpha^3 = 2\, C_M \psi\, [\, 0.5 - \chi\,]\, M^{1/2} \qquad (4)$$

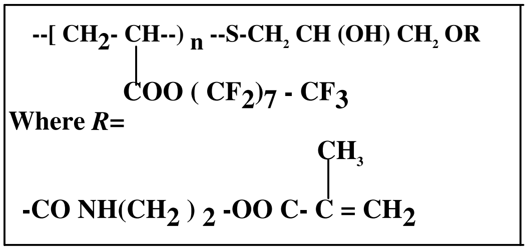
where, $\alpha = [\, \overline{r^2} / \overline{r_o^2}\,]^{0.5}$ and $\overline{r^2}$ and $\overline{r_o^2}$ are mean square end-to-end distances of the perturbed and unperturbed chain respectively, M being the molecular weight of the polymer. At $\chi >> 0.5$ as in the case of a perfluorocarbon/hydrocarbon copolymer in Fluorinert™ system, we have:

$$\alpha^5 - \alpha^3 = -\text{ve and } r < r_o \qquad (5)$$

when the dimensions of the polymer chain collapse to those smaller than the unperturbed polymer chain in a thermodynamically ideal solvent, resulting in the precipitation of the chain.

Method 2

This method of polymer particle generation in perfluorinated solvents involves the synthesis of latex particles of hydrocarbon core encapsulated by a perfluorinated polymer shell by dispersion polymerization of hydrocarbon monomers and acrylates. The dispersant used to stabilize the emulsion droplets is generally a macromer of a perfluorinated polymer soluble in the dispersion medium. The polymerizable end group is an acrylate as shown in *Figure 4* obtained by the reaction of Isocyanatoethyl methacrylate with the hydroxy terminal group of poly (perfluorooctyl methacrylate) which in turn was prepared by polymerizing the corresponding monomer in the presence of 3-mercapto 1,2-propanediol as a chain transfer agent:



$$-\!\!-[\,CH_2\text{-}\underset{\displaystyle COO\,(CF_2)_7\text{-}CF_3}{CH}\text{--}\,]_n\text{--}S\text{-}CH_2\,CH\,(OH)\,CH_2\,OR$$

Where R=

$$\text{-}CO\,NH(CH_2)_2\text{-}OO\,C\text{-}\overset{\displaystyle CH_3}{C} = CH_2$$

Figure 4. Structure of a Macromer comonomer stabilizer for Dispersion Polymerization of monomers

The organosol system is treated with pigments and charging agents and processed in a media mill to prepare toners. This method offers the advantage of a wide range of chemical composition to obtain the desirable properties for the toner films because of the versatility of the choice of monomers in the core.

Method 3

The type of perfluoromonomers listed in the *Figure 3* can be polymerized in Fluorinerts™ or other perfluorinated solvents in the absence of any hydrocarbon monomers and the soluble dispersants can be used to disperse pigments to prepare toners.

Surface Energy of Toner Films

The surface energy of the toner films are determined by the chemical composition of the polymers that bind to the pigment, the nature of the pigment surface and the amount of electrostatic charge on the toner particle. Thermodynamic work of adhesion of the toner film to various substrates is determined from the surface energies of the toner and the substrate[10]:

$$W_a = 2[(\gamma_s^d . \gamma_t^d)^{1/2} + (\gamma_s^p . \gamma_t^p)^{1/2}] \qquad (6)$$

With γ_s and γ_t being the surface energy of the substrate and the toner film respectively. The superscripts **d** and **p** refer to the dispersion and polar components of the surface energy. The surface energies in turn are obtained by contact angle measurements on the substrate surfaces with standard polar and nonpolar liquids. For the optimum degree of release of toner film (image) from the substrate and its transfer to the receptor surface, a balance of polar and nonpolar units in the binder becomes important. Incorporation of small amounts low surface energy monomers in the polymeric binders such as shown in *Figure 5* was found to be beneficial[9]:

$CH_2{=}C\text{-}\ COO(CH_2)_3\ Si\ [\text{-}\ OSi(CH_3]_3$
(Methacryloxypropyltris (trimethylsiloxy silane)

$C_3F_7O\ (C_3F_6O)CFCF_3CH_2OCOCH_2CH{=}CH_2$
(A Perfluoropolyether acrylate)

Figure 5. Low Surface Energy monomers

Interaction between overprinted toner layers as in the case of 4-color images can also be effected by having reactive functional groups in the dispersing resins. As an example, an amino group in the black layer can interact with a carboxyl group in the magenta layer to reduce cohesive failure between the layers during image transfer operations.[5]

Conclusion

A general description of liquid toner development was reviewed with reference to polyacrylic polymer particles in

Isopar™ and perfluorinated solvents of Fluorinert™ series as the low dielectric fluids. There are two main approaches to the preparation of toners. A straight forward approach involves the selection of monomers that yield soluble polymers in the solvent and at the same time adsorb onto the surface the pigment and provide solvated chains for the entropic stabilization of the particle. The toner particles are charged, usually positive either by adsorption of charging agents onto the particles or by charges built into the dispersant structure. For the toner to function effectively in imaging applications, the toner charge density as well as the adhesion characteristics of the toner film to the desired substrates and the dynamic mechanical properties of the pigment binder (dispersant) are required to be optimized. A second approach described is based on the synthesis of dispersed polymer particles by dispersion polymerization which bind to the pigment particles during the toner processing. These latex (organosol) particles being core-shell type, can be suitably tailored to the desirable mechanical properties for the toner films.

Liquid toners in perfluorinated solvents are novel with negligible prior art and this work provides an insight into the technology.

Acknowledgement

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Biography

S. Prabhakara Rao received his Ph.D in 1967 and worked for several years in academia in the areas of macromolecules, synthetic and biological both in India and the USA, He has worked for Halliburton Services (1981-84) in the area of enhanced oil recovery and Glidden-ICI coatings (1984-86) in pigment dispersions and paints. He has been with 3M Corporation since 1986 with research activities in the areas of Liquid toners, Receptor coatings and Inks. He is a Member of the IS&T and American Chemical Society. Contact author's e-mail address : sprao@mmm.com