Modified Pigments for Chemically Prepared Toner (CPT)

Joseph B. Carroll, Curtis Luke, Danny Pierre, Casey Whicher, Scott Sawrey, Angelos Kyrlidis, Jim Boswell; Cabot Corporation; Billerica, MA 01821, USA

Abstract

In the field of electrophotographic printing, the emergence of next-generation printing technologies such as chemically prepared toners (CPT) is changing pigment performance requirements. Every CPT processing technology has a unique set of performance requirements imposed on the colorant. In order to ensure optimum color performance, pigment particles (both black and color) must be well-dispersed and compatible within a host resin. The challenge becomes balancing dispersion quality and resin compatibility in the face of other environmental constraints such as transitions from solvent to water, pH changes, the presence of flocculating agents and surfactants, and large temperature ranges. Under these strict conditions, the ability to tune pigment surface properties (e.g. hydrophilic to hydrophobic, ionic to non-ionic, polymeric vs. small-molecule) to meet both improved color performance requirements as well as CPT processing constraints becomes very powerful. In response to these challenges, Cabot has developed several surface modification technologies that enable dispersions of pigments in aqueous and non-aqueous systems. In this presentation, we will highlight Cabot's portfolio of small-molecule and polymer modified pigments for improved performance in chemical toner systems. We will also discuss how the selection of carbon black morphology can influence key aspects of toner performance, such as color.

Introduction

The basis of toner consists of pigmented polymer particles that provide the appropriate image characteristics (optical density, color) after transfer and fusion to the paper. In non-magnetic toner carbon black has been the dominant black pigment. One of the major trends in the recent decade has been the shift to color printing which has created a demand for toner containing subtractive colorants (CMYK). Historically toner particles have been prepared by compounding the black and color pigments into the toner polymers followed by a grinding/classification process.

As the demand has increased for lower total cost of ownership and higher resolution printing, the toner industry has shifted its manufacturing processes to chemical processes. These processes incorporate the pigments into the polymer resin either by agglomeration in water or by polymerization in an organic phase surrounding the pigment particles [1]. This creates a challenge for both the toner formulators and the pigment suppliers, as the pigments need to remain dispersed in phases that are chemically very different without the application of any mechanical energy. Maintaining the dispersion quality of the pigments is critical to them delivering the optimal color and electrical performance in the toner.

In this paper we will discuss the various options that are accessible through Cabot's surface modification technology that allows flexibility in the preparation of toner. In addition, we will illustrate how changing the morphology and surface chemistry of carbon black can have an effect on the color properties of films simulating the printed page.

Surface Modification of Pigments

Over the past decade, Cabot Corporation has developed proprietary chemical modification technologies that can be used to alter the surface chemistry of pigments. One type of chemical modification technology utilizes diazonium salt intermediates to attach a variety of functional groups to carbon black and colored pigments [2]. The treating agent can be varied according to the application requirements. and can be ionic or non-ionic, hydrophilic or hydrophobic, small molecule or polymeric giving a lot of flexibility in terms of designing the pigment surface chemistry. These modifications are possible on the full range of color pigments used in digital imaging. For example, they can be used with cyan, magenta, red, and yellow color pigments and any carbon black. The modified pigments can be used either as is or in combination with commercially available polymers to open up a myriad of different options for tailoring the surfaces of the pigments specifically for targeted dispersibility and compatibility in either solvents or polymeric systems, as has been discussed in previous publications [3, 4].

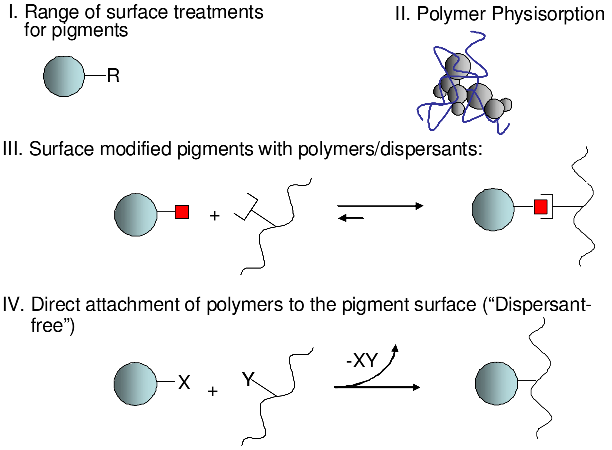

***Figure 1.** Cabot approaches to functional pigments for CPT*

Small-molecule diazonium treatments alone (Figure 1-I) can effectively tune the surface energy of pigment surface for improved resin compatibility with ranges of treatments that are hydrophilic, hydrophobic, basic, acidic, reactive, etc. There are also cases where select polymers can have high affinities for certain pigments in the absence of surface modification. However, polymer functionalized pigments (Figure 1-II) stabilized solely through physisorption, such as conventional dispersants, can become unstable during toner formulation testing and limited conventional dispersant solutions exist today for colored pigments. One way to prevent pigment agglomeration due to desorption of polymers from the pigment surface is to combine surface modified pigments with functional polymers (Figure 1-III). Here, complementary non-covalent interactions between surface modified pigment and polymer are used to enhance dispersion stability. In these systems, the resulting pigment dispersions will remain stable indefinitely until something begins to compete with the polymer-pigment interaction. In a system such as this, where toner formulations could compete with pigment-polymer interactions, Cabot has engineered a series of polymer modified pigments where the polymer has either been grafted to or directly reacted with the pigment surface (Figure 1-IV). Direct polymer attachment affords stable pigment dispersions with formulation flexibility.

Effects of Pigment Surface Chemistry on CPT Processes

From the pigment perspective we can classify the types of CPT processes into two general categories:

- Aqueous processes, such as Emulsion Aggregation (EA) [1], [5]
- Organic (solvent or monomer) processes, such as suspension polymerization of styrene acrylic based toner or preparation of polyester based toner using solvents such as ethyl acetate. [7]

In the following sections we will discuss advantages and disadvantages of different pigment surface chemistries for these two classes of CPT processes.

Aqueous processes

In typical EA processes, like those described in Ref. [1].[5] the pigments are dispersed in water using surfactants that can be anionic, cationic or non-ionic. This dispersion is then mixed with a stable latex emulsion of the polymer of interest. The two phases can then be agglomerated using a variety of different flocculation agents and the contiguous toner particle is formed by heating the system above the T_g of the toner polymer. The mixture is then cooled, washed to remove the surfactants, and coalescing agents, and finally dried to produce the toner powder.

An overview of the anticipated performance of Cabot's range of surface modified pigments in aqueous toner processing is shown in Figure 2. Pigments modified with strong acid groups will be readily dispersible in water over a range of pH, but may have difficulty agglomerating with the polymer latex and other ingredients in the agglomeration step of the process because of their outstanding dispersion stability in water. They may work best with resin latexes that are stabilized by similarly strong acidic groups. On the other hand, pigments modified with weak acid groups are more easily destabilized, because the stabilization can be easily disrupted with variations in pH [6] or the presence of multivalent ions, both known triggers for agglomeration in the EA process. A carefully designed pigment can have surface groups with pKa matching that of the polymer, thus allowing for coordinated flocculation.

	Surface Treatment	Water Dispersion	EA Process Performance	Toner Compatibility
Ionic	Strong acid	Good	Moderate	Moderate
	Weak acid	Good	Moderate	Good
	Strong base	Good	Moderate	Moderate
	[redacted]	[redacted]	[redacted]	[redacted]
Non-ionic	Hydrophobic small-molecule	Poor	Good	Good
	[redacted]	[redacted]	[redacted]	[redacted]
	Hydrophilic polymeric	Good	Poor	Good
	Hydrophobic polymeric	Poor	Good	Good

Figure 2. *Anticipated effects of pigment surface treatment on EA toner.*

Pigments with hydrophobic surfaces will by definition not disperse well in water without the assistance of surfactants. However, once these pigments are agglomerated and in the vicinity of the polymer in the toner particle, their surface chemistry can help compatibilize the pigment with the surrounding polymer thus providing improved dispersion quality in the final toner. Similar trends can be anticipated with polymer modified pigments. Pigments sterically stabilized with hydrophilic polymers will form stable aqueous dispersions that will remain unperturbed by most triggers of destabilization, and thus are not anticipated to get easily incorporated into the toner. Hydrophobic polymer modified pigments can be dispersed in water with the aid of surfactants and will behave similar to hydrophobic small molecule modified pigments in the toner.

The flexibility of the pigment surface design is a factor that can be considered in the troubleshooting and optimization of these toner making processes.

Organic Processes

In this class of processes the pigment is typically dispersed first into an organic solvent, monomer, or toner resin solution [7]. The organic dispersion is then mixed in water under shear and the organic droplets are then converted into toner particle either by polymerization of the monomer, by cross-polymerization of the polymer resin and/or by evaporation of the organic solvent. The pigments need to be well dispersed in the starting solvent and remain dispersed in the organic phase throughout the stages of toner particle formation.

Similarly to the aqueous processes, it is anticipated that pigments with different surface functionalities will behave very differently in this class of toner making processes. Very hydrophilic pigment surfaces are unlikely to yield successful toner, as the pigment is likely to prefer the aqueous phase. Pigments whose surfaces have been rendered hydrophobic will perform better, if the modified surface can retain its compatibility with the starting solvent and the final toner polymer.

Example: Dispersion in solvent

We present a few examples of the dispersion quality that can be accomplished with the modifications described above in Figure 1. Pigments in Table 1 have been modified with surface acid groups and then further modified with PO/EO containing polymers The dispersions in ethyl acetate (a commonly used solvent in polyester organic CPT processes) were prepared using 2mm glass beads in a Skandex paint shaker and filtered to remove the beads. The particle size measurements were conducted using a Nanotrac. It is apparent from Table 1 that the polymer alone cannot stabilize the pigment. Associating these polymers strongly with the acidic surface of the modified PR122 leads to an order of magnitude decrease in the mean particle size. Both EO-rich and PO-rich polymers yield comparably good dispersion performance.

Pigment	Surface	Mean particle size (nm) Solvent: EtAc
PR122	(I) Acid	1291
PR122	(II) EO/PO-1	1131
PR122	(III) Acid and EO/PO-1	132
PR122	(III) Acid and EO/PO-2	121

Table 1. *Effect of surface modification on pigment dispersion quality In ethyl acetate*

Example: Compatibility in polymer

The dispersions in ethyl acetate were let-down with solution of the polyester toner resin to prepare films that simulate the appearance of fused toner on paper. Typically, dispersions are letdown to prepare solutions of 20 wt% total solids of which 1% of the total solids is pigment. These solutions were then drawn down on glass slides to prepare films for further characterization.

These films were examined under an Olympus BX51 optical microscope to determine the compatibility of the modified pigments with the polyester resin. Images of a PR122 modified with the EO/PO-1 polymer via covalent attachment (route IV) are shown in Figure 3 below.

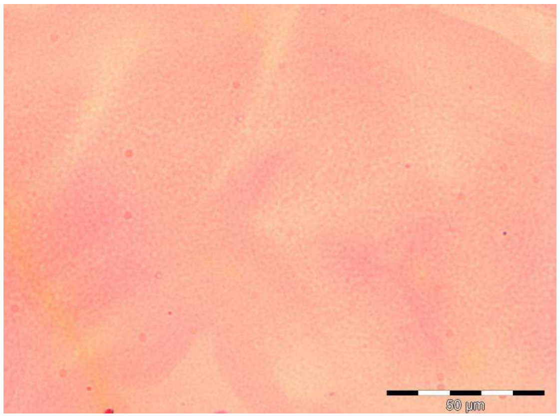

Figure 3. *Optical microscopy image of film containing PR122 with covalently attached EO/PO-1 polymer (via Route IV).*

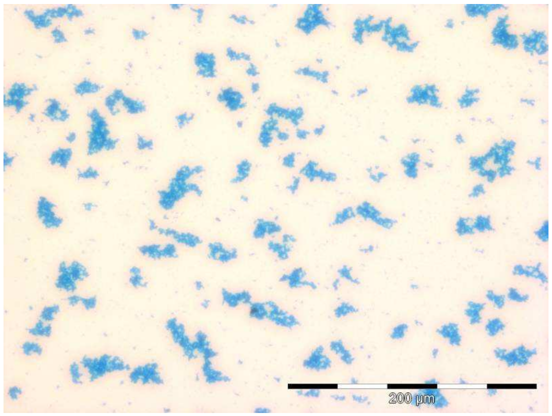

Figure 4*. Optical microscopy image of film containing PB15:3 modified with styrene acrylic polymer (via Route II).*

The type of attached polymer can have a significant effect on the compatibility of the modified pigment with the toner resin. For example, Figure 4 is a micrograph of a film containing PB15:3 modified with a styrene acrylic polymer which shows clear agglomeration of the pigment in the presence of the same polyester toner resin that was used in the film of Figure 3.

Effect of Carbon Black Morphology

Carbon black is the most prevalent black pigment in color toner formulations. In addition to the surface modification with diazonium salts, carbon black can be modified by oxidation which introduces non-specifically a variety of oxygen containing groups on the carbon surface. These groups can then interact with polymers in ways similar to those described in the previous section for modified pigments. In addition to the modification of its surface chemistry, the carbon black morphology can be altered to enhance some of the color characteristics of the toner.

In most pigmenting applications, utilizing higher surface area carbon black particles leads to improvements of the color properties of the final material, e.g. a coating or polymer composite. In the case of toner, and especially CPT-toner the situation is more complex, since higher surface area carbons are harder to disperse in various solvent systems and consequently their color performance may not be consistent with other applications.

Dispersion and Color Performance

Dispersions were first prepared using similar procedures as those described above. The dispersions were let down with commercial polyester toner resin to 20 wt% total solids. The solutions were then spin-coated on glass slides to prepare reproducible films with 2.1 µm thickness. The carbon black loading in the solutions that were spin-coated was such that the final films contained 10 wt% carbon black. The optical density of the films was measured against white paper using a Macbeth RD918 optical densitometer and the lightness (L*) was measured against white paper using a Hunter Lab Labscan XE colorimeter.

CB	Base CB Surface Area (m2/g)	Treatment	Mean particle size (nm) Solvent: EtAc
A	95	None	143
B	95	Oxidized	140
C	125	Oxidized	120
D	220	Oxidized	138

Table 2. *Effect of treatment and morphology on carbon black dispersion quality.*

CB	L* of films	Normalized OD (per 1 micron)
A	8.7	0.95
B	5.9	1.04
C	5.4	1.10
D	3.5	1.15

Table 3. *Effect of carbon black selection on color properties of polyester film containing 10 wt% CB.*

From the results in Table 2, we see that all four carbon blacks can be dispersed down to the aggregate size in the organic phase. In Table 3 we see that changing the surface chemistry of the carbon black can have an effect on the color properties of the films. Using an oxidized carbon black improved the lightness of the films and yielded a 10% improvement in the optical density of the films. In addition to the surface chemistry, increasing the base carbon surface area is also shown to have an effect. Doubling the surface area of the base carbon black led to an additional 10% increase in the optical density of the films.

Conclusions

The arrival of chemically produced toner technologies has enabled the next generation of printing technologies with an emphasis on print quality, color, and speed. Modification of the pigment surface chemistry allows the development of customized colorants that can meet the performance requirements of every step of the toner making process. Different chemistries may be needed in aqueous compared to organic solvent based CPT processes.

In the case of carbon black, the most commonly used black pigment in CPT, the flexibility allowed by surface modification of the pigment surface can be complemented by changes in the morphology.

References

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[5] See for example US patents 6,673,505 and 7,615,328.
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