Surface Modified Pigments for Improved Color in Chemically Prepared Toners

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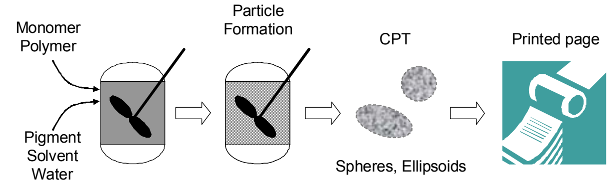
Abstract

In the field of electrophotographic printing, the emergence of next-generation printing technologies such as chemically prepared toners (CPT) is changing pigment performance requirements. In conventional toner manufacturing, high shear rates during compounding of the resin and pigment, followed by rapid solidification are necessary to ensure uniform dispersion. In contrast, most chemical toner processes do not rely on mechanical mixing to achieve good pigment dispersion in the toner. CPT processing occurs in the presence of multiple liquid phases. Under these conditions pigments can easily be separated from the resin. Without the benefit of high shear mixing and in the diverse environment of a multi-component CPT system, pigments must now balance ease of dispersibility with resin compatibility. Improving compatibility with the main components of a chemical toner allows the pigments to disperse and to remain dispersed throughout the entire CPT process (processes such as emulsion aggregation and direct polymerization). In response to these challenges, Cabot has developed several surface modification technologies that enable dispersions of pigments in chemical toner systems. In this paper, we will discuss how the improved dispersibility, compatibility, and processability of Cabot's modified pigments in toner resin dramatically improve the resulting color performance. Through proper design of the pigment surface, these benefits can be realized in any one of the well known chemical toner processes.

Introduction

Historically conventional toner particles have been prepared by compounding pigments into polymers, grinding the resulting compound and classifying toner particles. To enable higher resolution printing and to lower the total cost of printing, many toner manufacturers have begun adopting chemical toner processes, as illustrated in Figure 1 below.



Pigment Requirement:	*Dispersibility* *Stability* *Particle Size* *Compatibility* *SH&E*	*Processability* *Hydrophobicity*	*Dispersion* *Electrical* *Environmental* *Printability* *SH&E*	*Print quality* *Color*

Figure 1. *Steps in the preparation and use of a chemical toner and the requirements imposed on the pigment during each*

The evolution of electrophotographic printing from conventional toners to CPT requires improved performance of the base pigments in all stages of the CPT process. In these processes the pigments not only need to remain well-dispersed first in a liquid phase (water, solvent, or monomer depending on the process) but then must stay well-dispersed whilst being incorporated into a toner resin polymer either through an agglomeration process or through polymerization around the pigments. In both of these cases, there is no further dispersion of the pigment into the toner polymer. 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. Finding the right balance of good dispersibility across multiple, diverse liquid phases and maintaining compatibility in the final toner resin polymer directly impacts print performance. Figure 2 summarizes the relative improvements in image density, chroma, tribocharging, and overall ease of processing.

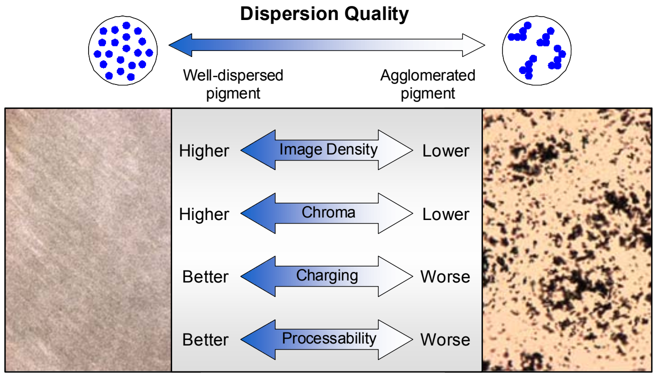


Figure 2. *Relationship between improved pigment dispersibility and resulting toner performance*

Previously, Kyrlidis et. al. have explored the sensitivity of carbon black compatibility to changes in host resin polymer properties. They showed that control of carbon black surface chemistry can enhance pigment dispersibility, improve resin compatibility and deliver better image density [1]. In this paper, we will present several advances in polymeric surface modification technologies that enable improved dispersions of colored pigments in chemical toner systems. We will then discuss how the improved dispersibility, compatibility, and processability of Cabot's polymer modified pigments in comparative toner resin testing dramatically improve the resulting color performance.

Surface Modification of Colored 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 reaction chemistry is summarized in Figure 3. The treating agent contains a functional group R, which can be varied according to the application requirements.

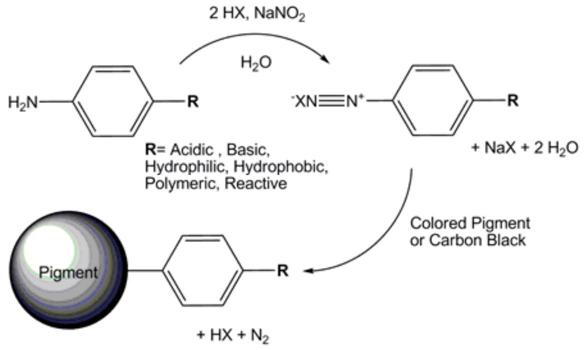


Figure 3. *Pigment modification using diazonium chemistry*

Using diazonium chemistries to modify the surface of pigments now presents a library of different options for tailoring the dispersibility and compatibility of pigments in a host solvent or toner resin system, see Figure 4.

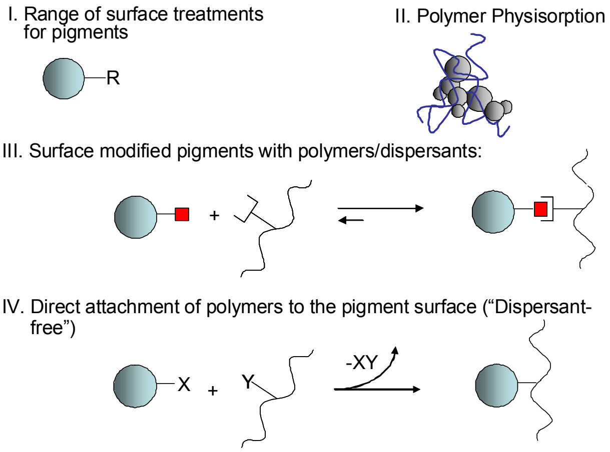


Figure 4. *Cabot approaches to functional pigments for CPT*

The treatment methods outlined above give us broad flexibility to match the pigment surface characteristics to the requirements of a specific chemical toner process. Small-molecule diazonium treatments alone (Figure 4I) 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 examples where select polymers can have high affinities for certain pigments in the absence of surface modification. However, polymer functionalized pigments (Figure 4II) stabilized solely through physisorption, such as conventional dispersants, can destabilize during toner formulation testing and limited conventional dispersant solutions exist today for colored pigments. Two approaches which we would like highlight in this paper are routes III and IV described in Figure 4. 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 4III). 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 4IV). Direct polymer attachment affords stable pigment dispersions with formulation flexibility. In this paper, we present a compatibility study of two Cabot approaches to polymer modified pigments (routes III and IV of Figure VI) versus conventional dispersant approaches (Figure II.) spanning three different colored pigments (PB15:4, PR122, and PY74), see Table 1.

Table 1. *Polymer modified colored pigments for model polyester toner resin compatibility testing*

Sample	Pigment	Route	Description
CYAN-Conv	PB15:4	II	Conventional
CYAN-1	PB15:4	III	Strong Association
CYAN-2	PB15:4	IV	Direct Attachment
MAG-Conv	PR122	II	Conventional
MAG-1	PR122	III	Strong Association
MAG-2	PR122	IV	Direct Attachment
YEL-Conv	PY74	II	Conventional
YEL-1	PY74	III	Strong Association

Colloidal Stability Testing and Preparation of Pigment-Polyester Films

In addition to standard colloidal stability testing (e.g. particle size, heat aging stability), multiple formulations of polymer modified colored pigment in ethyl acetate with a model polyester resin (Reichold Fine-Tone T-6694) were prepared. Polyester resin and color pigment dispersions dispersed in ethyl acetate were prepared at varying % pigment loadings from 1% to 6% pigment/resin ratios. The resulting formulations were then drawn-down onto glass slides and BYK-Gardner opacity charts using a 2 mil draw down bar (0.002 inches = 50 micron). Compatibility testing of each polymer functionalized pigment within the polyester resin was evaluated on from composite films on glass slides using an Olympus BX51 optical microscope. The resulting films' color was then analyzed from films let down onto BYK-Gardner opacity charts using a HunterLab spectrophotometer.

Optical Microscopy of Pigment-Polyester Films

Measuring compatibility between the polymer modified pigments in polyester resin using optical microscopy, although a qualitative approach, proved invaluable in determining which routes were most promising (see Figure 5).

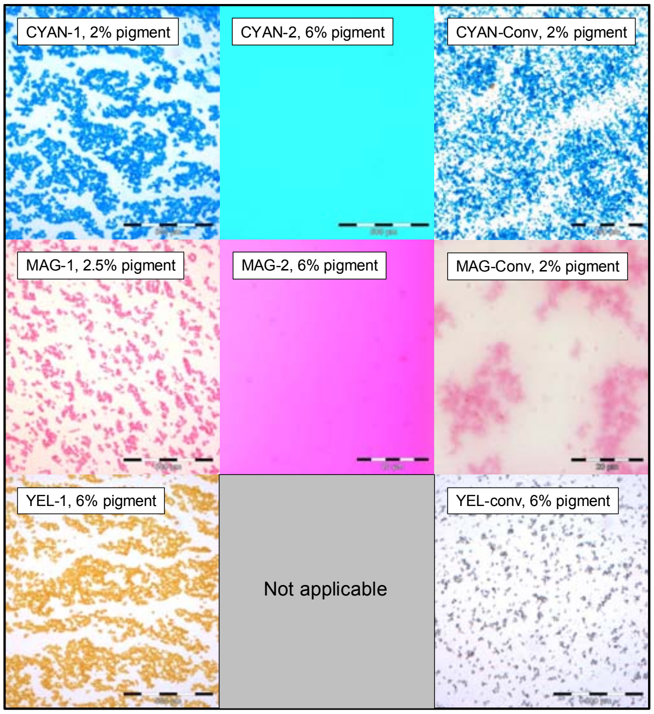


Figure 5. *Optical microscopy images of polymer modified pigments in model polyester resin at varying % pigment loadings*

As is shown in the optical microscopy images in Figure 5, pigment compatibility within the polyester resin is quite varied depending on the polymer modification route chosen. In all cases, routes II (using conventional dispersants) and routes III (strong association) show varying degrees of pigment agglomeration in the polyester let down films. All pigments tested with conventional dispersants showed both poor dispersion in the polymer film and poor dispersion alone in ethyl acetate with particle sizes > 500 nm. In contrast, polymer stabilized pigments using route III have been shown to have excellent dispersion properties alone in solvent (particle sizes < 200 nm); however, in the presence of the competing polyester host resin, the pigment agglomerates. The most robust polymer modified pigments presented are ones prepared using Route IV. Direct attachment of polymers to the pigment clearly offers the advantage of good dispersion in solvent alone (particle sizes < 200 nm) as well as good dispersion in the resulting dried polyester films. These "dispersant-free" covalently attached, polymer modified pigments show excellent compatibility in the Reichold T-6694 resin as well as many other systems not discussed today. Being able to sustain good pigment dispersion during the formation of the dry polyester films (which we use as our model CPT process) has direct consequences on the resulting films color performance.

Color measurements of Pigment-Polyester Films

After compatibility testing, we evaluated the color of the polyester films containing polymer modified pigments using a HunterLab spectrophotometer (see Figure 6). The color data details the L*a*b* coordinates of all of the polymer modified pigment/polyester composites at varying % pigment loadings.

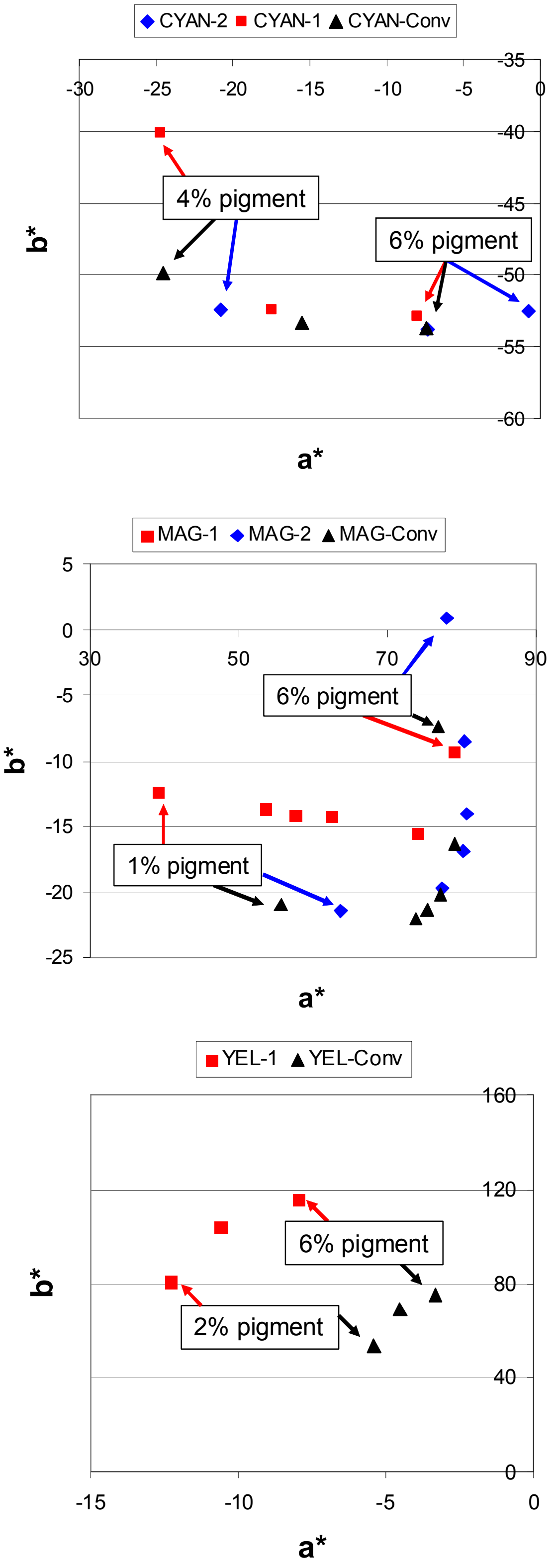


Figure 6. *Plots of L*a*b* space of polymer modified pigments in model polyester resin at varying % pigment loadings*

Mirroring the results from the compatibility testing, films prepared from Route IV polymer modified pigments showed the best color performance. For cyan and magenta, direct attachment of polymer to the pigment surface yields larger chroma values at lower % pigment loadings (see Figure 7).

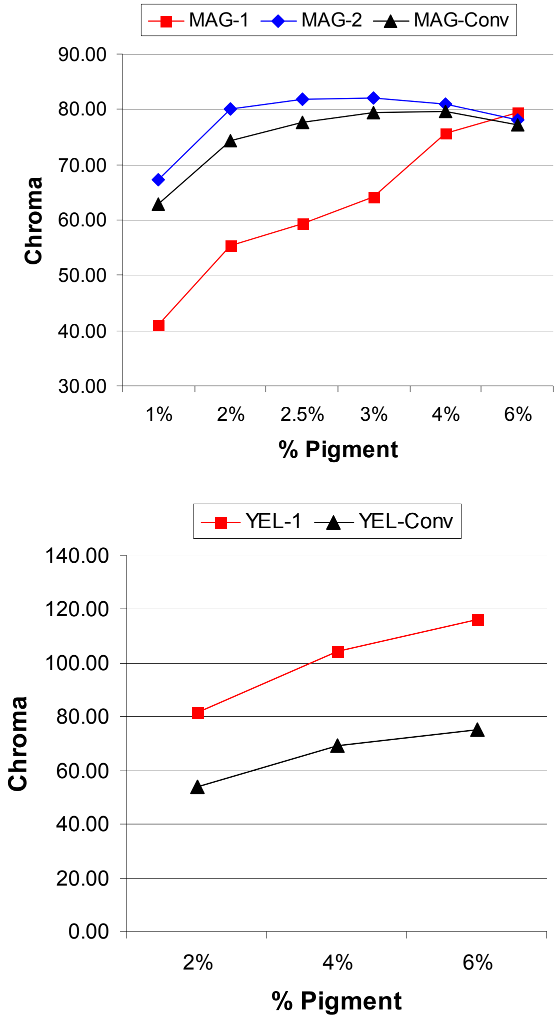


Figure 7. *Chroma values of polymer modified pigments in model polyester resin at varying % pigment loadings*

In addition to improved chroma, direct attachment of polymer to the pigment surface improves color gamut. Cabot's "dispersant-free" magenta dispersions were able to access much warmer tones of magenta (yellow shade), not possible with conventional dispersants. Similarly, "dispersant-free" cyan dispersions were able to access the most neutral tones of cyan (negligible a* contribution), not possible with conventional dispersants. And finally, despite agglomeration in the polyester films, Cabot's polymer-dispersed PY74, YEL-1, shows a dramatic chroma improvement of almost 40 units compared with conventional dispersant sample YEL-Conv resulting in brighter, more vivid printed images.

Conclusions

Cabot has developed several surface modification technologies that enable dispersions of pigments in chemical toner systems. The resulting improvements in the dispersibility, compatibility, and processability of Cabot's modified pigments in toner resin dramatically improve the resulting color performance.

References

[1] A. Kyrlidis, A. Shim, "Designing Pigments for Optimal Performance in Chemical Toners" 24th International Conference on Digital Printing Technologies and Digital Fabrication 2008 Pittsburgh, Pennsylvania;September 8, 2008; p. 72-74

[2] US Patents 5,554,739 and 5,922,118.

Author Biography

Joseph B. Carroll received his BS in Chemistry from Merrimack College (2000) and his PhD in Organic Chemistry from the University of Massachusetts-Amherst (2005) He worked as a Research Assistant Professor at Clemson University (2005-2006) developing colloid based photonic and light-emitting materials before joining Cabot Corporation in 2006. His work has focused on the development of new surface modified pigments (specifically colored pigments) for a variety of applications, including toners and chemically prepared toners (CPT).

Joshua H. Chase received his BS in Biology from Roger Williams University (1996). He has worked as a research associate for ITW TACC and has owned a prototype machining company. He joined Cabot in 2006 and has worked on toner applications and composite materials.

Trung C. Truong received his BS in Chemistry from Brown University (2006). He joined Cabot Corporation in 2007 and has focused on the development of new surface modified pigments and carbon blacks for a variety of applications, including black matrix, toners and chemically prepared toners (CPT).

Angelos Kyrlidis received his Diploma in Chemical Engineering from the National Technical University of Athens, Greece (1987) and his PhD in Chemical Engineering from the Massachusetts Institute of Technology (1993). He worked at the Lawrence Berkeley Laboratory and Molten Metal Technology before joining Cabot Corporation in 1998. His work has focused on the development of new surface modified pigments for digital imaging applications, including toners.

Eilidh Bedford received her Ph D in Polymer/Materials Science from Cambridge University. She has worked at Unilever in the UK and in the US as head of physical science and then in areas of formulation and delivery at biomaterials start ups. She now heads development in Performance Segment at Cabot, with particular responsibility for displays and toners.