Polymeric Surface Modification of Pigmented Colorants and Applications to Digital Printing

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Abstract

Novel pigment colorant sets have been developed using Cabot's proprietary surface treatment technology. The new technology involves treatment of the pigment surface with reactive precursors. Subsequent secondary and tertiary reactions with pre-formed polymers and oligomers yields materials with unique physico-chemical properties. The combination of unique chemistries and advanced purification methods lead to well characterized pure pigments, void of free polymers and impurities.

These methods allow customization of the pigment surface that can create new levels of pigment performance required for demanding digital printing applications. This includes enhanced formulation flexibility, new levels of colloidal stability, tuned colorant-media interactions, and increased permanence. A discussion of the various chemical approaches and material performance properties will be presented.

1. Introduction

In order to meet the performance demands required for pigmented inkjet colorants in the areas of color, formulation flexibility, and colloidal stability, Cabot has been developing a next generation of materials. Recently Cabot introduced a matched set of surface modified color pigments for inkjet applications.[1] These materials extend the utility found in surface treated carbon black to the relevant color pigments for inkjet.

The increasingly challenging requirements in areas of inkjet print speed, durability, and reliability at lower drop weights require a different approach and are the subject of this paper. Cabot is now developing a new generation of inkjet colorants using its proprietary diazonium chemistry to generate pigments with reactive precursors. The secondary and tertiary reactions of these precursors yield products with both unique and useful properties.

2. Pigment Surface Modification Chemistry

Cabot's proprietary surface treatment technology enables the chemical attachment of a wide variety of functional groups to the surface of pigments (Figure 1).[2] This chemistry has allowed Cabot to develop a versatile toolbox of surface treated colorants (Figure 2).

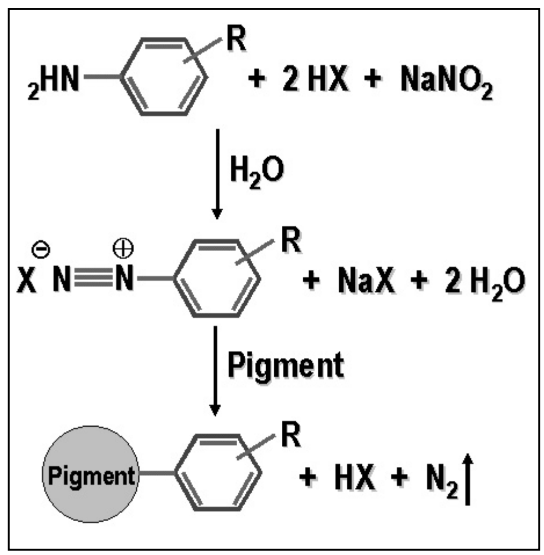

Figure 1. Surface treatment via diazonium chemistry

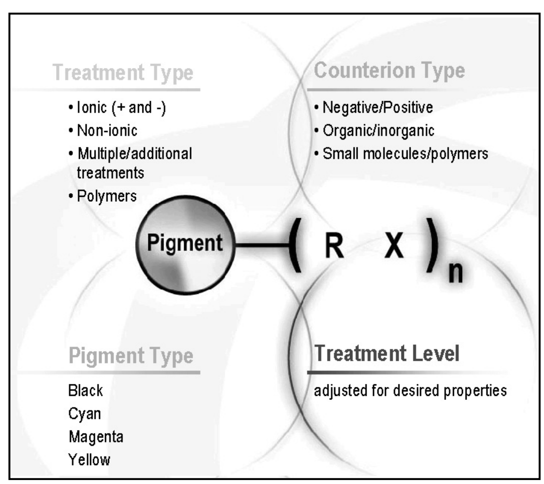

Figure 2. Surface Treatment Versatility

In contrast to conventional dispersions CaboJet™ colorants incorporate a stabilizing group that is covalently bound by chemical attachment through carbon-carbon bonds (Figure 3). This paper will discuss developments in two areas in which Cabot is using reactive precursors as a chemical "hook" in order to do secondary and tertiary surface chemistry (Figure 4). The second group introduces the desired properties. Therefore it is now possible to attach groups that are not compatible with diazonium chemistry. There are many variants to this chemistry, dependent on the initial treatment path:

- Condensation reactions
- Coupling reactions
- Addition-elimination reactions
- Displacement reactions, Etc...

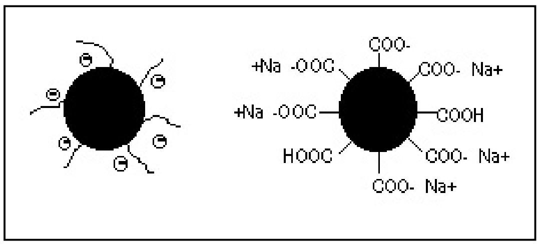

Figure 3. Conventional vs. CaboJet™ surface modified pigments

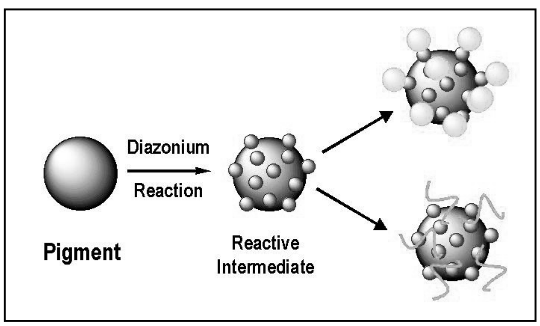

Figure 4. Secondary surface chemistry

A preferred reactive precursor group, attached using water based diazonium chemistry is the aminophenyl-sulfoethylsulfato group (APSES, Figure 5). This reactive moiety is often used as the active portion of reactive dyes for textile applications. Using APSES as the electrophilic base, it is possible to attach a variety of nucleophilic materials to the surface of the modified colorant such as:

- Polyamines
- Polyethylenimine
- Polyols
- Polyvinyl alcohol
- Sorbitol
- Sugars and Polysacharides
- Gelatin
- Amino alcohols
- Polyethyleneglycols
- Polypropyleneglycols

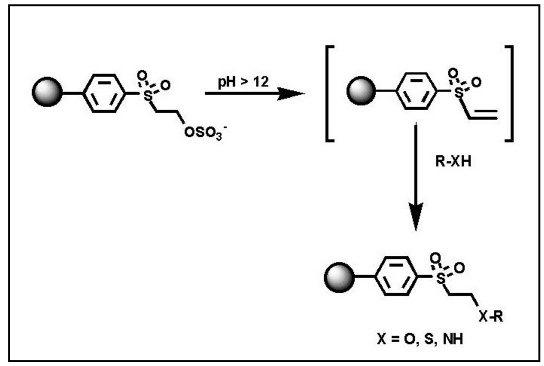

Figure 5. Reactive path for APSES with nucleophiles

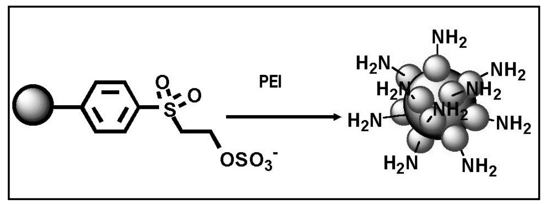

Figure 6. Synthesis of polyamine surface treated carbon black

Table 1. Properties of PEI treated Carbon Blacks

Polyamine	PEI 1800	PEI 1200	PEI 600
% Polymer	9%	8%	7%
UPA mV (nm)	151	162	184
Print OD	1.25	1.28	1.37
ICB	Excel.	Excel.	Excel.
Waterfastness	5 min.	1-5 min.	1-5 min.
Highlighter Smear	Excel.	Excel.	Good

The product of APSES treated carbon black and branched polyethylenimine (PEI, Figure 6) yields a material with a number of interesting properties including improvements in intercolor bleed and waterfastness (see Table 1).

The nucleophile type and level can be varied based on the requirements of the specific application.

The reactive primary polyamine surface allows the reaction with a number of electrophilic equivalents such as:

- Anhydrides
- Acid chlorides
- Lactones
- Active esters
- Alkyl halides
- Vinyl sulphones
- Polystyrene co-acrylic acid
- Polyacrylic acid

An example of this tertiary chemistry is the condensation of carboxy containing polymers such as styrene acrylics via dehydration yielding a stable amide linkage (Figure 7). Dispersions from this class of materials yields inkjet dispersions with improvements in the following properties:

- Smear resistance
- Waterfastness
- Rub resistance
- Media independence

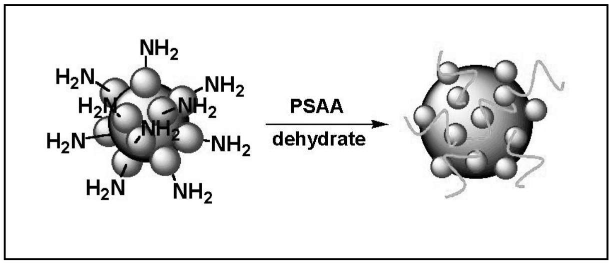

Figure 7. Condensation reaction of a p-styrene acrylic polymer

3. Conclusion

Diazonium surface modification chemistry, which has been developed by Cabot, enables the preparation of pigments, both black and color, with novel surface chemistry for inkjet applications. The ability to covalently anchor polymers to the pigment surface opens new possibilities for the synthesis of pigments with enhanced properties required for the increasing demands in the digital printing industry.

4. References

1. Yu, Y. and von Gottberg, F. "Surface Modified Color Pigments for Ink Jet Ink Application" IS&T Sixteenth International Conference on Advances in Non-impact printing Technologies, October 2000, Vancouver, BC.
2. US Patents 5,554,739 and 5,922,118.

Biography

Dr. Mark Kowalski received his B.S. Degree in Chemistry from the College of William and Mary in Virginia in 1983 and a Ph.D. degree in Organic Chemistry from the University of Utah in 1988. He has worked for DuPont as a Researcher in the Corian® Business (1988-1993) and Hewlett Packard in the Ink Jet Supplies Business as an ink chemist and project manager (1993-2000). He joined Cabot Corporation in 2000, where he is the Technology Manager for the Ink Jet Colorants Division.