Surface Modified Color Pigments for Ink Jet Ink Application

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Abstract

A novel color pigment dispersion set has been developed for ink jet ink applications. The approach utilized proprietary technology to modify the pigment surface by attaching functional groups, which are chosen to impart the desired physiochemical properties for the systems. The need for conventional dispersants is eliminated for water based applications when ionic and/or ionizable groups are attached to the surface. This proprietary method is analogous to that used in commercially available CAB-O-JET® 200 and CAB-O-JET®300 black pigment dispersions, which provides pigments with enhanced formulation flexibility and superior stability. The new dispersion set comprise surface modified Copper Phthalocyanine blue pigment (**IJX™253,** PB 15:4), Quinacridone red pigment (**IJX™266,** PR 122), and Monoazo yellow pigment (**IJX™273,** PY 74). Other examples will be presented as well. By employing this surface modification technology, we are able to produce a color pigment dispersion set with high surface tension (> 70 dynes/cm), low viscosity (< 3 cP at 10% solids), small particle size, and reliable long term stability, while providing unprecedented formulation latitude and retaining the inherent permanence properties of the color pigments.

1. Introduction

Inkjet printers have become familiar products in homes and offices by virtue of their versatile nature at an affordable price. Industrial inkjet printing applications are expected to grow rapidly based on the need for digital customization. As inkjet technology advances, so too have the requirements for reliable inkjet inks, which are expected to provide photo quality color with great permanence and media independent properties at smaller drop volumes.

When inkjet printers were first introduced almost all the inks were dye based. Today with the introduction of pigmented black inks, carbon black has been accepted as the black colorant of choice[1]. The successful use of carbon black colorants in inkjet inks has gone a long way to dispel misconceptions about the inherent stability and reliability levels that are achievable using pigmented colorants.

Pigments have many inherent advantages over dyes as inkjet colorants. In printing applications that require permanence properties, such as waterfastness, light fastness, and rub resistance, pigmented colorants are preferred. While carbon black pigments are now widely being used in inkjet inks, color pigment usage has been limited to wide format printing applications. It is anticipated that SOHO (small office home office) customer expectations for prints with a high degree of permanence and photo quality color will drive the demand for pigmented color inks possessing the following properties:

- **Rich color (hue and chroma)**: Unlike carbon blacks, which are inherently darker (higher OD) than black dyes, color pigments generally lack the color strength of dyes, especially on plain papers. On coated/special media, pigmented colors more closely approach the color gamut of dyes.
- **High quality pigment dispersions**: A fundamental requirement of pigments used in inkjet inks is exceptional colloidal stability, high purity and no unwanted large particles. These stringent pigment requirements are required to provide a reliable ink that will work in lower and lower drop volume printing heads.
- **Formulation flexibility**: Inkjet inks are carefully engineered systems that contain many components. A constant struggle among ink formulators is to find ink additives that do not interfere with each other or with the colorant. Desirable properties of the pigmented dispersion would include high surface tensions, low viscosity and an absence of impurities that may effect the ink formulation.

Commercially available color pigment inks, including Encad GO™ ink and KODAK PROFESSIONAL™ pigmented inks, rely on conventional dispersant technology. In these inks, color pigments are milled or subjected to other forms of shear in the presence of suitable dispersants to yield pigment dispersions with the desired particle size distribution and colloidal stability. The addition of polymer or surfactant as dispersants has some inherent limitations including:

- **Formulation limitation**: Conventionally dispersed pigments containing surfactants or polymer dispersants generally have low surface tension and high viscosity. Ideally the pigment dispersion would have properties much like water, allowing the ink formulator the flexibility to adjust the surface tension and viscosity to the desired level. Also, the pigment dispersant could potentially interfere with other ink components and subtle changes in the ink or its environment may cause the dynamic equilibrium between the adsorbed and free dispersant to be shifted.

- **Poor stability**: There are very stringent stability requirements for inkjet inks, particularly those for SOHO applications. Many available conventional color pigment dispersions do not meet these requirements.
- **Particle size restriction**: A pigment dispersion with small particle size is considered important for both color and stability. Dispersions of small pigment particles require larger amounts of surfactant to stabilize and this constrains formulation flexibility.
- **Contamination**: Metal grinding media often leads to metal contamination.

This paper will describe a novel color pigment dispersion set (**IJX™ 253**: PB 15:4; **IJX™ 266**: PR 122; and **IJX™ 273**: PY 74) for aqueous inkjet ink applications. Unlike conventional dispersions, our products rely on charged functional groups that have been chemically attached to the pigment surface to provide electrostatic stabilization. As a result this new pigment dispersion set does not contain any external dispersants. Cabot's pigmented dispersions have surface tension and viscosity similar to those of water and are compatible with a wide range of inkjet ink additives. The proprietary[2-5] technology described in this paper enables Cabot to manufacture color pigment dispersions with favorable properties for inkjet ink applications. During the following discussion we will demonstrate the physical properties of our products and the flexibility of our surface modification technology.

2. Color Pigment Surface Modification Chemistry

Cabot Corporation possesses proprietary surface treatment technology that enables us to chemically attach a wide variety of functional groups to the surface of pigments. In this paper, our discussion will focus on ionic functional groups, for example $-SO_3^-$ (sulfonate), $-COO^-$ (carboxylate), or R_4N^+ (quarternary) groups. When these groups are introduced to the pigment surface, they impart electrostatic stabilization to the aqueous pigment dispersion. As a result the need for external dispersants is eliminated. The method used to modify the color pigment is analogous to that used to produce commercially available CAB-O-JET® 200 and CAB-O-JET® 300 black pigment dispersions[2,3]. After the chemical treatment, by-products and other impurities can be efficiently removed via methods such as ultra-filtration and the unwanted large size particles can be removed via centrifugation, filtration, or similar means[6]. The final products can be further purified through ion-exchange processes to remove di-valent ions that are free in solution or on the pigment surface.

3. Characteristics of Surface Modified Color Pigment Dispersions

Surface modified organic pigments offer great freedom to the inkjet ink formulators or developers by providing dispersions with high surface tension, low viscosity, good co-solvent compatibility, and excellent colloidal stability. Furthermore, we are able to demonstrate that our products and surface modification process does not alter the chromagenic or other properties of the starting pigments. Pigments described in the following sections are surface modified with sodium sulfonate groups.

3.1 General Physical Properties

Table 1 summarizes the physical property data for a set of color pigments produced by attaching sodium sulfonate groups to the pigment surface. Characteristic features are high surface tension (> 70 dynes/cm) and low viscosity (< 2.5 at 10 % solids) with mean volume particle sizes around 100 nm. Pigments with sulfonate groups are stable over a wide pH range (3-10). By attaching carboxylate groups to the surface a pigment set can be produced that is only stable at higher pH (> 7). Techniques are available to further reduce the particle size if so desired.

Table 1: General physical properties

Physical Properties	IJX™ 253	IJX™ 266	IJX™ 273
Pigment Type	Cyan PB 15:4	Magenta PR 122	Yellow PY 74
Pigment Loading	11.7 %	10.4 %	9.2 %
Viscosity[1]	2.1 cP	2.4 cP	2 .0 cP
Surface Tension[2]	70.3 dynes/cm	71.8 dynes/cm	72.0 dynes/cm
pH	6.9	7.6	6.4
Particle size[3]	91 nm	105 nm	137 nm

[1] Shell #2 Efflux Cup
[2] Kruss Digital Tensiometer K-10
[3]Mean volume particle size determined by Microtrac® Ultrafine Particle Analyzer (Honeywell)

3.2 Superb dispersion stability

The dispersion stability of surface modified color pigments was quantified by monitoring the change in mean volume particle size (as determined by Microtrac® Ultrafine Particle Analyzer (Honeywell)) and the number of particles greater than 0.5 microns per ml of dispersion at 15 % solids (as determined by AccuSizer Model 780 available from Particle Sizing Systems NICOMP, Santa Barbara) over a period of time. The sulfonated pigment set was evaluated with or without the addition of 2-pyrrolidone (2-P). We chose 2-P as a surrogate ingredient for a co-solvent compatibility study. Samples were aged over a 4 month period at low temperature (10 °C), room temperature

(RT), and high temperature (70 °C). In Table 2 to Table 4, "**Pigment**" refers to 10% pigment dispersion, "**2-P**" refers to a pigment dispersion with 5% pigment and 10% 2-P.

Table 2: Aging test (4 month) of IJX™ 253 (**PB 15:4**)

PB 15:4	Mean volume particle size (nm)[1]		Number of particles > 0.5 µm[2]	
	Initial	**Aged**	**Initial**	**Aged**
10 °C: Pigment	92	86	2.7E+8	8.6E+7
2-P	89	91	2.4E+8	1.1E+8
RT: Pigment	-	92	-	1.1E+8
2-P	-	90	-	1.6E+8
70 °C: Pigment	-	91	-	1.8E+8
2-P	-	90	-	1.6E+9

Table 3: Aging test (4 month) of IJX™ 266 (**PR 122**)

PR 122	Mean volume particle size (nm)[1]		Number of particles > 0.5 µm[2]	
	Initial	**Aged**	**Initial**	**Aged**
10 °C: Pigment	110	107	3.8E+8	1.5E+8
2-P	105	102	4.0E+8	1.0E+8
RT: Pigment	-	106	-	1.4E+8
2-P	-	106	-	1.4E+8
70 °C: Pigment	-	94	-	1.5E+8
2-P	-	100	-	1.3E+8

Table 4: Aging test (4 month) of IJX™ 273 (**PY 74**)

PY 74	Mean volume particle size (nm)[1]		Number of particles > 0.5 µm[2]	
	Initial	**Aged**	**Initial**	**Aged**
10 °C: Pigment	135	130	1.6E+8	4.8E+7
2-P	125	112	1.7E+8	6.3E+7
RT: Pigment	-	135	-	5.8E+7
2-P	-	126	-	1.3E+8
70 °C: Pigment	-	130	-	1.3E+8
2-P	-	105	-	5.0E+7

[1]Mean volume particle size is determined by Microtrac® Ultrafine Particle Analyzer (Honeywell)

[2]This was determined by Accusizer Model 780 available from Particle Sizing Systems NICOMP, Santa Barbara

Clearly, Cabot's surface modified pigment dispersions showed excellent colloidal stability under these testing conditions.

3.3 Printing performance/color gamut

Each of the surface modified color pigments was formulated into a generic ink and printed onto a set of plain papers with a commercially available thermal inkjet printer. Table 5 illustrates some general print properties. All these inks showed excellent transparency when printed onto transparency films. Since we are chemically modifying the pigment surface, it was important to demonstrate that the surface modification process does not alter properties, like lighfastness and color gamut, which are inherent to pigments. The properties presented in Table 5 are comparable with previously reported values for inks prepared with conventional pigment dispersions and appear unaffected by the surface modification.

Table 5: Printing performance of modified pigments

		L*	a*	b*	OD	WF[1]	LF[2]
IJX™ 253	PB 15:4	52	-18	-37	1.0	24 hrs	90%
IJX™ 266	PR 122	56	47	-9	1.0	5 min	93%
IJX™ 273	PY 74	89	-6	84	1.2	5 min	<50%

L*a*b* readings were determined with a Hunter LabScan II instrument

[1] Time taken for print to dry sufficiently that the runoff of 2.5 ml of DI water contains no colorant.

[2] LF: lightfastness expressed by % OD retention after 400 hrs of continuous UV-A irradiation using a Accelerated Weathering QUV/SE Instrument (Q-Panel Co).

4. Technology Flexibility

As indicated by many of the granted patents and published patent applications filed by Cabot relating to the pigment surface modification, the chemistry and post-processing steps are flexible and versatile. During the following discussion we will briefly summarize the major variables of our technology and their impact on the performance. Obviously, the flexibility of our technology enables us to tailor our products for specific requirements and applications.

4.1 Different Functional Groups

The ability to introduce different types and amounts (attachment levels) of functional groups onto the pigment surface represents a key feature of our technology. Surface properties of color pigment particles can therefore be tailored through the surface modification process. Such tailored surfaces can be designed to specifically interact with ink or media components and provide a means to enhance permanence and other print properties. Table 6 shows that surface charging characteristics, as measured by zeta potential, can be controlled (in sign or magnitude) by varying surface attachment level or treating agent.

Table 6: Zeta-potential of surface functionalized PR 122

Surface functional groups	Zeta potential[1]
Sulfonic acid salts: High attachment level	-35 mV
Sulfonic acid salts: Medium attachment level	-25 mV
Sulfonic acid salts: Low attachment level	-18 mV
Quarternary salts	+ 20 mV

[1] As measured using ZetaPlus, Zeta Potential Analyszer from Brookhaven Instruments Corporation, Holtsville, NY in 1mM NaCl

Print properties can also be affected by attaching different functional groups or moderating the attachment level. For example, inkjet inks containing color pigments with surface carboxylate groups (COO-) show improved waterfastness over the inks containing a pigment with surface sulfonic acid modifications.

4.2 Different Counter Ions

Each charged surface group has associated with it a counterion within the double layer. The counterion can easily be varied through an ion exchange process. Table 7 shows how the sodium counterion on a carboxylated PB15:4 pigment can be effectively converted into a potassium or ammonium counterion. In the case of introducing an ammonium counterion, a clear impact on waterfastness is observed. Since the surface groups are attached to the pigment surface we are not constrained by the presence of a dispersant that may have a higher selectivity for the ion exchange resin and hence desorb.

Table 7: Ion-exchange (I/E) carboxylate sodium salt modified PB 15:4

	Na (ppm)	NH_4 or K (ppm)	WF [1]
Before I/E	6000		1 hr
After NH4 I/E	90	4800	10 min
After K I/E	100	10300	-

[1] Time taken for print to dry sufficiently that the runoff of 2.5 ml of DI water contains no colorant.

4.3 Purity

Impurities present a serious concern in inkjet, especially in thermal inkjet printers. By using purification methods such as ultrafiltration and ion exchange technology we can effectively remove water soluble and charged impurities from these dispersion[6].

4.4 Other Pigments

Our surface modification technology has been successful in treating a wide range of pigment classes, such as metal phthalocyanines, quinacridone, naphthol-AS, mono-azo, di-azo, and diketopyrrolo-pyrrole types of pigments.

5. Conclusion

Surface modification chemistry, which has been developed by Cabot, enables the production of a novel color pigment set for inkjet ink applications. As it has been demonstrated in this paper, when color pigment surfaces are modified with ionic groups, stable pigment dispersions with favorable physical characteristic can be achieved for aqueous inkjet ink. In addition, the versatility of our modification chemistry and post-processing afford us extensive latitude in providing products with specific functional groups and properties.

6. References

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Biography

Dr. Yuan Yu received his B.S. Degree in Chemistry from the Peking University in China in 1990 and Ph.D. degree in Organic and Material Chemistry from the University of Minnesota in 1996. He joined Cabot Corporation in 1998 and has since focused on the technologies for nano-particle surface modification.

Dr. Friedrich von Gottberg received his B.S. Degree in Chemical Engineering from the University of the Witwatersrand in South Africa in 1990 and MSCEP and Ph.D. degrees in Chemical Engineering from the Massachusetts Institute of Technology in 1992 and 1997, respectively. He joined Cabot Corporation in 1997 and has focused on the scale-up and commercialization of surface modified pigments.