Pigment Surface Modification via Nucleophilic Treating Agents

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Abstract

Employing chemical reactions that modify particle surfaces to impart desirable physical-chemical properties has enjoyed enormous commercial success. One example is the surface modification of pigment particles for inkjet inks. As the applications of pigmented inkjet inks continue to grow, there is a need to modify a wider range of pigment types. The existence of many classes of pigments with various functional groups has presented challenges for the development of a general chemistry that can react with any pigments. As a result, inventing new ways of modifying pigment surfaces is important. In this report, treating agents having nucleophilic groups were used to modify Pigment Green 36 (PG36). When PG36 was modified with nucleophiles bearing water-soluble groups, pigment particles became water dispersible. Dispersions showed excellent colloidal stability and the color properties of PG36 have not been affected. This paper will also discuss the versatility of this chemistry for introducing a wide range of functional groups onto pigment particles that possess leaving groups.

Introduction

With the advancement of nano-technologies and their applications, there is an increasing demand for high performing nano-particles. Improvements in functional performance and formulation flexibility have been the main drivers. One of the most common ways to achieve those goals is through particle surface modification. Such modification introduces specific chemical groups to particle surfaces to provide desirable performance yet maintain the integrity of the particles. Particle surface modifications have been practiced for over a century now and are widely used in many industrial applications. For example, Carbon Black particles can be oxidized by nitric acid to introduce polar and ionizable groups to their surfaces so that they can be mixed easily into water or other polar media. Organic color pigment surfaces can be modified directly or through other incorporation methods so that they can be made compatible with the media they will be put into. In the past 20 years, one class of nano-particles, namely, pigment particles, has increasingly been used in many demanding applications, for example, in inkjet inks [1]. Inkjet inks are highly engineered products and pigmented inkjet inks have to meet stringent performance and colloidal stability requirements.

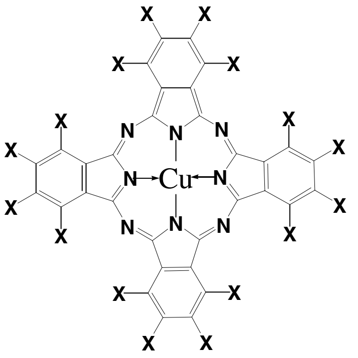
Pigmented inks are now widely used in inkjet applications [1-3] with stability and reliability performance matching dye based inks. When inkjet printers were first introduced almost all the inks were dye based. Today there are many OEM products that are using pigment and many next generation products will continue the trend of displacing dyes. Pigmented colorants now being used in inkjet inks have overcome many of the nozzle reliability problems that originally prevented their widespread adoption.

As the adoption of inkjet continues to expand so too are the requirements for high performing pigmented colorants. One of the growth areas is to provide pigmented inkjet inks with primary colorants in addition to cyan, magenta, and yellow colorants. This trend is primarily driven by the popularity of printing digital photograph with an expanded color gamut, for example, inkjet printers on the market now are using red and blue to accompany C, M, and Y. We expect the future need will also include Orange and Green. In addition to that, there have been a plethora of patents using inkjet technology to fabricate color filters for LCD application [4], which use primary colors of Red, Green, and Blue. Due to the structure variety of different classes of color pigments, one chemistry can effectively modify one type of pigment may not be as effective to modify other types. As a result, there is an on-going need to develop specific chemistries to surface modify specific class of pigment particles.

This paper will discuss applying nucleophilic substitution reaction to modify pigment particles that have leaving groups in their molecular structure. Examples of those pigments are Pigment Green 7 (PG7), Pigment Green 36 (PG36), and Pigment Yellow 138 (PY138). All of those pigments contain halogen-leaving groups in their structure. Chemical structures of PG7 and PG36 are depicted below. Specifically, this paper focuses on surface modification of PG36. As stated above, a high performing green pigment dispersion can find applications in hexachrome printing and color filters.

There are considerable challenges to develop colloidally stable PG36 dispersions. Due to the large content of bromine atoms in the PG36 chromophore, the pigment has a very high intrinsic density of nearly 3 g/cc,(nearly double most of the other organic pigments). High particle density implies that in order to achieve the same degree of colloidal stability against settling, PG36 particle size has to be considerably smaller than other types of organic pigments. Furthermore, most technologies to stabilize pigment particles are based on electro-static stabilization by introducing ionizable groups onto the pigment surface. According to DLVO theory [5], higher charge density (zeta potential) is required to stabilize smaller particles. As a result, a process of modifying PG36 that yields small particle size with higher charge density is needed.

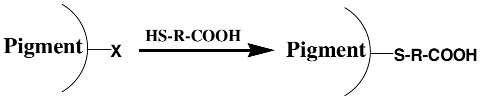
There have been several patent publications that disclose the use of nucleophilic reaction to modify PG7 or PG36 [6]. However, none of those modifications yield water dispersible products for aqueous inkjet application. Specifically, this paper discusses two types of nucleophilic reactions: a thio reaction and sulfite reaction. The sulfite chemistry has not previously been used to modify



PG 7: Majority X= Cl
PG 36: Majority X= Br

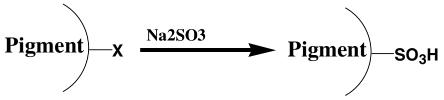
pigment surface. In addition, this paper will also discuss the impact on color and colloidal properties by those modification chemistries. Those two general reaction schemes are shown below.

Thio reaction



X = Cl or Br R = Alkyl and Aryl

Sulfite Reaction



Experiments

PG7 and PG36 were obtained from Sun Chemical and all other chemicals were from Aldrich and used without purification. Elemental analysis was performed by a contract lab. The viscosity was measured using a Shell-cup available from Norcross Corp, Newton ,Mass. Zeta potential was determined using Zeta Plus (available from Brookhaven Instrument Corp. in Holtsville, N.Y.) in 1 mM KCl and 1 mM HCl electrolyte solutions. The mean volume particle size of the dispersion was measured by the dynamic light scattering method using a MICROTRAC Ultrafine Particle Analyzer (available from Honeywell, Minneapolis, Minn.). Colloidal stability of the dispersion was studied by heat aging the material at 70° C, for 24 hours and particle size both before and after heat aging were recorded. Detailed reaction and purification conditions can be found in US 6,641,653.

Result and Discussion

Thio Chemistry

PG36 was reacted with 3-mercaptobenzoic acid (3-MBA) in DMF at 125 degree C for 60 hrs. The green solid from the reaction was washed and then dispersed into di-water. This dispersion was dialyzed using a 50 KMWCO membrane. Properties of the resulting dispersion are listed below. Mean volume particle size of this dispersion had been successfully reduced to 80 nm by more intensive sonication.

Table 1: Analytical Data of 3-MBA Modified PG36

% Solid	11.00%
Vicosity	1.3 cP
pH	7.0
Surface Tension	72 dynes/cm
Zeta: pH 3	(-11) mV
Zeta: pH 7	(-30) mV
Potassium	1.53%
Sulfur	2.56%
mv	120 nm
Change of mv after 1 day 70 C	2%

Similar to other small molecule surface modified pigment dispersions [7], 3-MBA modified PG36 yielded water like viscosity and surface tension. Those characteristics have been demonstrated to provide great formulation latitude for inkjet inks.

The sulfur analysis indicated that roughly 12% of the "Br" has been replaced by the 3-MBA, (roughly translates to about one molecule of 3-MBA for every PG36 molecule.) Since PG36 was not soluble in the reaction solvent, the PG36 molecules on the surface must have been modified to a greater extent. The obvious question is "has this process produced dye molecules?" In order to demonstrate this modified green pigment dispersion contains pigment but not soluble colored species such as dyes, the dispersion was ultra-filtered through different molecular weight cut off (MWCO) membranes (Microsep membranes available from Pall Filtron Corp. Ann Arbor, Mich.). Control experiments showed that green dye molecules could easily pass through 5 KWOCO membrane. The resulting filtrates were examined for the presence of color. The observations are shown in Table 2.

Table 2: Soluble Colorant in the Dispersion

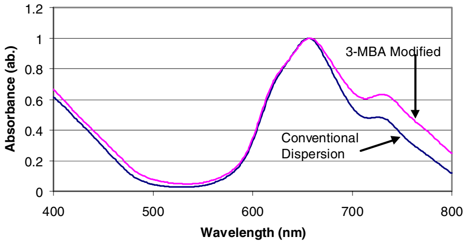
MWCO of Membrane (dalton)	Color of Filtrate
5,000	Clear
50,000	Clear
100,000	Clear
300,000	Very lightly Green

The results show that the modified green pigment prepared in this example did not contain soluble colored species since very little color was observed in the filtrates, even when using a very high MWCO membrane. The product is a pigment, which is further supported by the particle size and zeta-potential results shown in Table 1.

Additionally, the molar ratio between Sulfur and Potassium is about 2:1, which is consist that at pH 7 only ½ of the carboxylic acid groups have been neutralized [8].

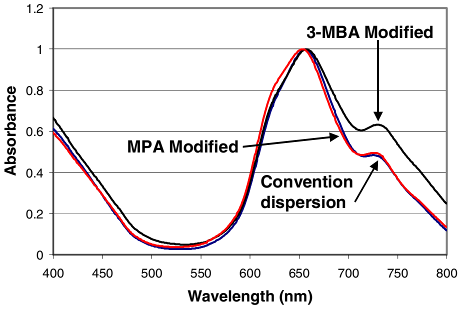
Another related question is the impact of this modification on color properties of PG36. As stated above, PG36 molecules on the surface had been modified extensively with 3-MBA, which could potentially shift colors due to the electron donating thio-phenyl group. UV-vis of the 3-MBA modified PG36 dispersion was compared with a conventionally surfactant stabilized PG36 dispersions at similar particle size. Normalized spectra are shown in Figure 1. As indicated, the surface modified PG36 did show more absorption at longer wavelength around 530 nm, which is consistent with the modification chemistry.

***Figure 1**. UV-vis of PG36 Modified with 3-MBA*



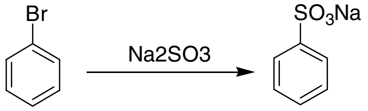
In some applications this type of color shift is not desirable. A new treating agent with little-to-no impact on color properties needed to be identified. A literature search indicated that according to Woodward Rules, -OCH3 has a color shift of 13.5 nm and –O-phenyl has a color shift of 51.5 nm. Even though this is not a direct comparison for thio, it clearly indicates that the phenyl group contributes greatly to the color shift. PG36 was then modified with 3-mercaptopropionic acid (3-MPA), at similar attachment levels and the particle size the color shift was observed to be minimized as seen in Figure 2 below.

***Figure 2**. UV-vis of PG36 Modified with 3-MBA and 3-MPA*



This thio reaction had been tested on PG7 and PY138.In both cases stable and surface modified dispersions were obtained.

Sulfite Chemistry



Sulfite chemistry has been known for years and it is a commodity chemical and broadly used in many industrial and consumer applications. It is also known in the literature that sodium sulfite can be used to react with bromo benzene to replace bromo groups with sulfonic acid groups [9]. According to author's literature search, there has been no example of using this simple chemical reaction to modify pigment particle surface.

After PG36 was treated with sodium sulfite in a pressurized reactor, the green product was washed and redispsered into DI-water. Green dispersions were further purified by dialysis against DI-water using a 50KWOCO membrane. The resulting dispersions showed similar viscosity, surface tension, and particle size as in Table 1. However, the attachment level as measured by Na was much lower (0.1%). Na level is indicative of colloidal stability. Understandably, the dispersions were not as stable as those in Table 1. The nucleophilic reaction can be catalyzed in the presence of Cu(II) salt [10]. A further reaction with CuSO4 as catalyst greatly improved the attachment level, Na increased to 0.3% and S increased to 0.43%. This dispersion gave similar colloidal stability as those shown in Table 1. Additionally, unlike the thio chemistry above, the molar ratio between Na and S is close to 1:1 which is consistent with the fact that sulfonic acid is a strong acid and at pH 7, all acid should have been neutralized. The Sulfite reaction is a very simple chemistry and it can be further optimized to increase yield and efficiency.

Summary

Due to the complex nature of color organic pigments, it is necessary to develop specific chemistry to take advantage of specific functional groups on the pigment structure. This paper illustrated using nucleophilic reactions to modify pigments that possess leaving groups. Our initial work showed that those reactions could be successfully applied to prepare pigment dispersions which show a high degree of dispersability and colloidal stability. In some cases, surface modification will have a negative impact on properties such as color, but those issues can be addressed through the application of a mechanistic understanding of color shifting properties of chemical groups. Chemistries explored and discussed in this paper can be used to introduce other functional groups that can facilitate the introduction of additional functional groups and polymers [11].

References:

[1] US Patent 5,554,739.

[2] US Patent 5,554,739.

[3] US Patent 6,398,858.

[4] US Patent 6,084,006

[5] Elimelech M.; Gregory J.; Jia, X. and Williams, R.A. *Particle Deposition and Aggregation*, published by B&H, **1995**.

[6] US Patent 5,851,280; 4,824,948; 5, 788, 914; and 5,705,101

[7] Yu, Y. and von Gottberg F., "*Surface Modified Color Pigments for Inkjet Ink Application*" Page 512-515, *IS&T 16th International Conference*, October 2000, Vancouver, Canada.

[8] Yu, Y. and von Gottberg F., "*Titration of Surface Modified Pigment Particles*" Page 769-772, *IS&T 20th International Conference*, October 2004, Salt Lake City, Utah

[9] Jerry March. *Advanced Organic Chemistry*, published by J&W, 4th Edition, **1992, Page 656**

[10] Bowman, *Tetrahedron Letter*, **1984**, 25, 5821

[11] US 5,554,739; 5,707,432; 5,837, 045; 5,851,280, and 6,042,643, and PCT Publication WO 99/23174.

Author Biography

Dr. Yuan Yu received his B.S. Degree in Chemistry from 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 his initial focuses were on the technologies for nano-particle surface modification and characterization. Recently, he is leading activities in commercialization of surface modified pigments for inkjet ink applications.

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