Polymeric Dispersants with Specific Affinity to Pigments for Ink Jet Applications

Alex Shakhnovich; Joseph Carroll; Darryl Williams; Cabot Corporation; Billerica, Massachusetts/USA

Abstract

A new class of highly effective polymeric dispersants for inkjet applications have been developed by covalent attachment of organic chromophore groups, capable of interacting with pigments, to hydrophilic polymers. The anchoring effect of such groups is defined by molecular similarity to the pigment structure and by less specific interactions. The affinity of the chromophore to the colorant surface is amplified by connecting multiple groups to one polymer molecule. Dispersants based on styrene-acrylic or styrene-maleic anhydride polymers with attached azo dyes proved to be very effective for yellow azo pigments, such as PY74, providing inkjet compositions with very high resistance to ink formulations with multiple co-solvents and reduced particle settling. On the other hand, a quinacridone chromophore, being linked to certain hydrophilic polymers, produces a very versatile dispersant, suitable for quinacridones, phthalocyanines and Carbon Black. Synthetic pathways to new dispersants as well as properties of obtained inkjet materials are discussed.

Introduction

For certain pigments, creation of stable inkjet dispersions presents a number of challenges. One of the widely described approaches includes usage of pigment derivatives (PD) or crystal growth inhibitors with ionizable groups[1,2]. These are supposed to have high affinity to the pigment surface due to structure similarity and therefore stay adsorbed on the pigment surface. These are generally low-molecular weight compounds, similar in structure to the pigment which the PD is targeted to disperse. Although this approach does provide pigment dispersions, there is an equilibrium between the dissolved and adsorbed PD which can lead to dispersion failure. Dissolved PD may cause resistor fouling in thermal inkjet systems. Furthermore, in aggressive ink formulations the adsorption equilibrium can be perturbed by surfactants and humectants displacing the PD from the pigment surface, increasing these problems. Humectants and penetrants such as micelle-forming 1,2-hexanediol (HD) or triethylene glycol monobutyl ether (TEG MBE) are believed to be very aggressive in this respect. This can lead to dispersion and/or printhead failure. Cabot's surface treatment technology for color pigments, based on diazonium chemistry, generates pigment derivatives also. Such a treatment technique may generate intercalated PDs, which are not so easy to desorb. Cabot has shown that diazonium treatment of PY74 goes by a different route[3], and the obtained dispersion may suffer more from surfactants and humectant action as described above than other, similar, dispersions.

Principle

In this article we use the term ***conjugate*** to define the polymers with attached pigment derivatives. We conceived the idea that covalent attachment of several PD to an ionizable polymer may produce a much more effective dispersant than PD or polymer alone. It is postulated that desorption of a PD anchored through the polymer chain to other adsorbed PD's will be less favorable compared to PD which is not polymer bound, due to entropy effects. Although the structural similarity of the PD to the molecular structure of the pigment generally aids affinity, we have discovered that it is not a requirement – for example flat polycyclic structures may have high affinity to Carbon Black or copper phthalocyanine also.

Polymers

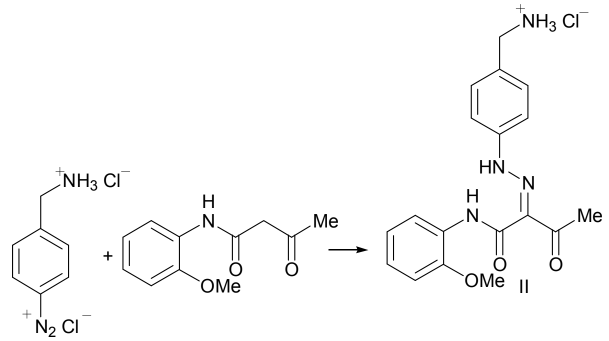
The most common types of polymers used as pigment dispersants in InkJet applications, are copolymers containing units of acrylic or methacrylic acid as ionizable groups. The acid number of such polymers may be between 80 and 250. A typical example of these polymers is a styrene-acrylic Joncryl ® resin (Ia). Also commonly used are hydrolized styrene-maleic anhydride (SMA) colopymers (Ib) (Eq. 1). Many SMA polymers, such as SMA3000®, are available from Sartomer.

(1)

Both groups of polymers usually contain hydrophobic units, such as styrene or α-methylstyrene and may also have side chains to further control hydrophilicity/hydrophobicity balance.

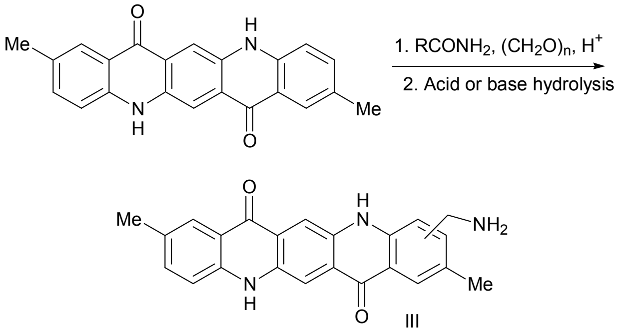
Pigment derivatives

We have found that although condensation of PD with acid-containing polymers can be achieved by many synthetic approaches, reaction of amine-containing PD with an activated or nonactivated carbonyl group is preferred. Aminated pigment



(2)

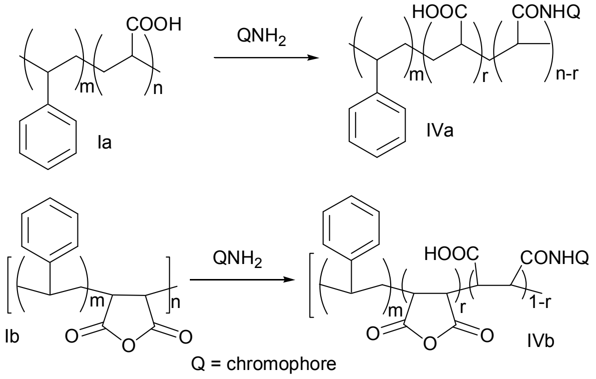
derivatives based on azo chemistry can be obtained by direct synthesis (Eq. 2). Here it is convenient to use aminobenzylamines as diazo components. Due to the higher basicity of the aliphatic aminogroup compared to the aromatic aminogroup, the aminomethyl group remains protonated and therefore intact in PD (II) over the course of diazotization and coupling. Another approach to PD synthesis uses pigment aminomethylation[4] with a mixture of paraformaldehyde and amide, followed by acid or base hydrolysis – this reaction is especially suitable for polycyclic and heterocyclic pigments, such as quinacridones, indolinones or phthalocyanines (Eq.3). In both cases the aliphatic aminogroup provides a convenient link for connection to the carboxylated polymer.



(3)

Synthesis of Conjugates

Any of several methods for carbonyl group activation may be employed if needed. If the aminated PD is stable enough, condensation between the carboxylated polymer and aminated PD can be achieved by simple heating in aprotic solvent, such as N-methylpyrrolidone. SMA polymers are especially suitable for this modification due to the high anhydride reactivity, providing an extra carboxy group. This reaction does not require a catalyst. (Eq. 4)



(4)

Proof of Attachment

Gel-permeation chromatography has been employed to demonstrate the attachment of chromophore to the polymer. Simultaneous detection by refractive index (presence of polymer) and by UV-VIS at the chromophore wavelength (presence of chromophore) allows estimation of the coupling efficiency.

Pigment Dispersions with Conjugates

Many different combinations have been evaluated, and several of them showed quite interesting dispersing properties. Specifically conjugates of azo colorant II with SMA polymers turned out to disperse PY74 and Carbon Black very well. On the other hand the conjugates of (aminomethyl)-2,9-dimethylquinacridone (AmDMQA, III) with both Joncryl ® and SMA polymers are excellent dispersants not only for quinacridones, such as PR122, PV19 and PR202, but also for copper phthalocyanine (PB15) and Carbon Black. The versatility of these dispersants supports the earlier statement that structure similarity of the chromophore of PD to the pigment is not entirely necessary. All dispersions were prepared using either a rotor-stator high shear mixing device or an attritor mill with zirconium silicate beads by combining the pigment, conjugate polymer, water and necessary amount of base needed to ionize some or all of the carboxy groups of the polymer. The ratio pigment:conjugate was between 1:0.15 to 1:1 and excess of non-adsorbed conjugate was removed using membrane filtration. After this dispersions were centrifuged to remove coarse particles and later concentrated to 10-15% solids using membrane filtration again. The technique had been applied to CMYK pigments used in Inkjet, such as PY74, PR122, PB15:4 and Carbon Black. Dispersing ability of conjugates was much better than the corresponding polymers without attached PD's and generally the median particle size of dispersions was between 100 and 180 nm, depending on the pigments and conjugates used[5].

Performance in InkJet Applications[5]

Obtained dispersions at 4-6% pigment loading were subjected to heat aging in presence of two most aggressive ink components – HD and TEG MBE, added in the amount of 10% by weight. It is clear that the stability of dispersions increases dramatically versus the control - hydrolized SMA3000 (Table 1).

Table 1. Heat aging of obtained dispersions

Polymer	Chromophore	Pigment	Heat aging with solvents		
			Particle size initial, nm	Particle Size, 1 week at 70 C, nm	
				HD	TEG MBE
SMA3000	II	PY74	165.2	175.1	160.7
SMA3000	III	PR122	150.5	160.1	158.9
SMA3000	III	PB15:4	130.3	135.4	135.3
SMA3000	III	Carbon Black	105.1	112.3	112.7
SMA3000	none	PR122	140.3	crashed	crashed

Corresponding ink formulations obtained with conjugate-dispersed CMYK pigments were all stable. We were able to reliably print these inks using both piezo and thermal platforms. All prints were of high quality, with good saturation and, what is very important, had good smear- and highlighter resistance due to the presence of polymer. There was no need to add an additional binder.

Conclusions

A new class of custom pigment dispersants has been designed, prepared and evaluated. Attaching chromophores with high affinity to the pigment surface to ionizable polymers enables the preparation of inkjet dispersions with good heat aging and printing properties.

References

[1] T. Ishigama, T. Oshiba *et al*., "Pigment Yellow 74 and printing ink composition", Eur. Pat. Appl. EP 1,316,588 A2, (2003)

[2] H. Matrick, "Pigment toners with improved transparency", US Patent 4,561,899; (1985).

[3] A. I. Shakhnovich, "Dispersant chemistry gives up its secrets", Eur. Coatings J., issue 6, p. 28, (2006).

[4] H. Zaugg, W. Martin, "α-Amidoalkylation at carbon" in Organic Reactions, vol. 14, p. 52, (1965)

[5] A. I. Shakhnovich, D.S. Williams, J. B. Carroll "Inkjet ink compositions comprising polymeric dispersants having attached chromophore groups" US Pat. Appl. Publ. US 2007 179,213, (2007).

Authors Biographies

Alex Shakhnovich received his MS in Chemistry in 1972 from Moscow State University and his PhD in Heterocyclic Chemistry (1979) from Institute of Dyes and Intermediates (Moscow, Russia). He had been working in different academic and industrial institutions in Russia and US, including Clariant and General Electric. Since 2002 he is a Principal Scientist at Billerica, MA R&D center of Cabot Corporation. His research interests include synthesis, surface modification and application of organic colorants.

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).

Darryl Williams was educated at the University of Delaware (1989) and Massachusetts Institute of Technology (1993), where he received his Ph. D. under the 2005 Nobel Laureate in Chemistry. He has authored 19 scientific articles and 10 US Patents in the fields of materials, catalysis, nanoparticles, lighting, and polymers. A focus of much of his work at both General Electric and Cabot has been on the interaction of materials with light, using light as a probe of structure and using materials to generate light.