Polymeric Dye Inkjet Colorants with High Waterfastness

Mihaela Madaras, Donald Diehl, Steven Link, Shari Eiff, Wanda Swartz, and John DiCillo; Eastman Kodak Company, Rochester, NY/USA

Abstract

Ink compositions used in inkjet printers can be classified as either pigment based, in which the colorant exists as pigment particles suspended in the ink composition, or as dye based, in which the colorant exists as a fully solvated dye species that consists of one or more dye molecules. Commonly used dye-based inks suffer poor waterfastness and low durability against wet rub abrasion, which can render text and universal packaging code information illegible. A subclass of dye-based inks may contain polymeric colorants in which a chromophore is covalently bound to a polymer structure. This presentation describes our work with a class of polymeric colorants that can be utilized in ink compositions for inkjet printing that are stable, do not adversely affect the performance of an inkjet nozzle, and deliver images with high waterfastness.

Introduction

Current inkjet ink colorants are either dyes or pigments [1]. Dyes are colorant materials fully soluble in solvents at the molecular scale. Pigments are particulate materials in the size range of nanometers to micrometers that are insoluble in the carrier fluid. Perceived color from molecularly dissolved dyes arises through selective photon capture by the magnetoelectronic molecular environment governed by allowed quantum physical rules of electron promotion. Perceived color from dispersed pigment particles also includes dye-like direct light absorption as well as other light interactions: diffraction, reflection, and refraction. Light scattering by pigment particles can be reduced by milling the pigments to a very small size, i.e., less than 100 nm [2]. However, this decreased scatter is achieved at the cost of increased time and energy in the expensive milling process. Solid pigment particles generally interact with a broader range of light wavelengths than dissolved dyes so relatively broader light absorbance and lower molar absorptivity spectra are commonly displayed by even the smallest pigment particle dispersions.

While dyes generally have more visually intense colors than pigments, this comes at a price [3]. Dyes for inkjet inks are commonly soluble in water. Water-based inkjet inks employing soluble dye colorants tend to have poor waterfastness, i.e., the image sharpness and density is decreased by the application of water to the medium upon which the image is printed. In contrast, inkjet inks employing pigment dispersions generally lose little or no colorant when subjected to water treatment and are thus said to have high waterfastness.

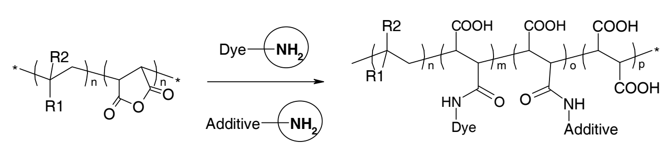
Pigment-based inks are often preferred over dye-based inks because they possess better waterfastness and better resistance to light and gas, especially ozone, as compared to printed images with dye-based inks. However, pigment-based inks have a number of drawbacks. Great lengths must be undertaken to reduce a pigment to a sufficiently small particle size and to provide sufficient colloidal stability to the particles. Pigment-based inks often require a lengthy milling operation to produce particles in the submicrometer range needed for most modern ink applications. If the pigment particles are too large, light scattering can have a detrimental effect on optical density and gloss in the printed image. Pigment inks are also difficult to jet through inkjet printheads having small nozzle diameters, e.g., less than 25 μm, and numerous approaches have been taken to formulate pigment-based inks for piezo and thermal inkjet printheads.

Self-dispersed pigment-based ink compositions lacking a film-forming polymer binder offer high optical density on untreated bond papers that approach electrophotographic-printing quality, with values of about 1.4 [4]. The colorant, however, is readily redispersed by wet rub abrasion, resulting in undesirably low durability. Polymer-dispersed pigment ink compositions offer excellent waterfastness, wet rub durability, and dry rub abrasion on all substrates, but optical density suffers on plain papers, where the colorant apparently wicks along the cellulose fibers into the interior of the paper, leading to lower density printed text [5].

Based on the contrasting properties of dyes and pigments listed here, we found a need for novel materials that have the intense color and versatility of water-soluble dyes, offer high optical density when printed on a wide range of papers, including bond, and at the same time have excellent waterfastness.

Design of Polymeric Colorants for Inkjet

The polymeric colorants presented here are based on maleic anhydride copolymers as the reactive backbone [6]. They easily react with aliphatic amines, making them amenable to attaching different moieties, such as dyes and additives that function as property "modulators." Thus, the design of these molecules becomes flexible and allows for adjustment of color, water solubility/dispersability, viscosity, etc.



Maleic anhydride copolymer Polymeric colorant

Scheme 1. *Synthesis of polymeric colorants.*

The resulting polymer contains carboxylic groups that can be neutralized with different bases to become water soluble.

Examples of bases used to neutralize these polymeric colorants are: potassium hydroxide (KOH), triethyl amine, dimethylethanol amine, methyldiethanol amine, and triethanol amine.

The dyes incorporated into this polymeric structure can belong to many classes of dyes with the condition that they have the reactive amine functionality and they are at least partially soluble in the reaction mixture.

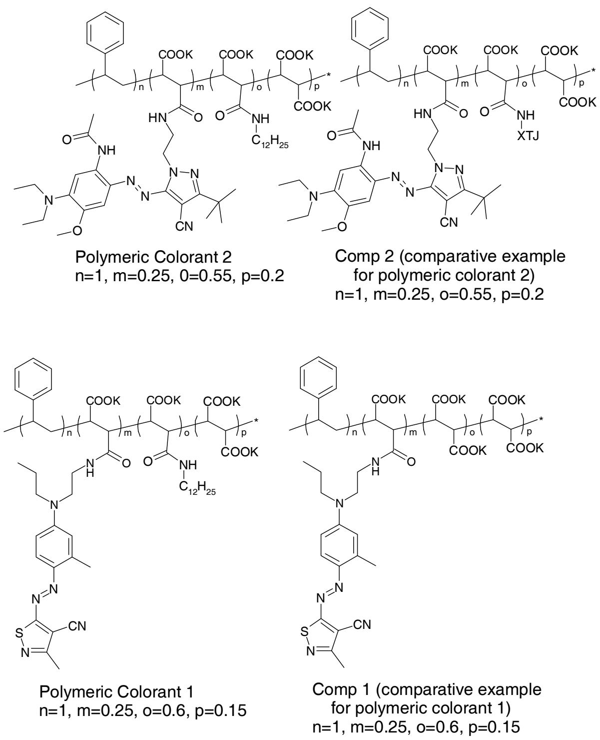
The additives attached to the polymers are materials that modulate the waterfastness and optical density when printed on paper, more specifically, that modify the overall hydrophobicity of the polymeric colorant. The additive is usually a primary aliphatic amine, substituted or unsubstituted, branched, linear or cyclic alkyl group, having from about 2 to 24 carbons. Thus, not only by changing the ratio of the additive to the dye but also by changing the size and structure of the hydrophobic group, one can modify the hydrophobicity. The additive group is critical in attaining excellent waterfastness and optical density on bond papers.

Waterfastness of Polymeric Colorants

As the data in Table 1 shows, the presence and nature of the additive group have a decisive effect on waterfastness. This effect is consistent throughout a wide range of bond papers described in Table 2. Comparative example 1 lacks the dodecyl (additive) group relative to polymeric colorant 1, whereas comparative example 2 contains a PEO-PPO polyether (Jeffamine XTJ-506) fragment instead of the hydrophobic dodecyl group. In both comparative examples the absence of the dodecyl group has a negative impact on the waterfastness results. The patches printed with polymeric colorants lost almost nothing in optical density and behaved very much like printed pigment inks. All inks in Table 1 were formulated at 5% conc of polymeric colorant, 11% humectant level, and printed with a Canon S520 desktop inkjet printer. The waterfastness test consisted of exposing the printed image to running water for 1 min and measuring the optical density before the test and after the paper had dried.

Table 1. Waterfastness results on several papers

Receiver	% Optical Density Loss			
	Polymeric Colorant 1	Comp 1	Polymeric Colorant 2	Comp 2
Receiver 1	1	16	2	31
Receiver 2	0	37	1	35
Receiver 3	0	47	2	41
Receiver 4	1	14	2	22
Receiver 5	1	5	2	23
Receiver 6	1	0	0	32
Receiver 7	2	45	1	39
Receiver 8	1	65	N/A	N/A
Receiver 9	3	54	1	53
Receiver 10	1	10	0	17
Receiver 12	1	26	2	35
Average loss (%)	1.09	29.30	0.75	34.07



***Scheme 2**. Structures of polymeric colorants in Table 1.*

Table 2. Receiver description

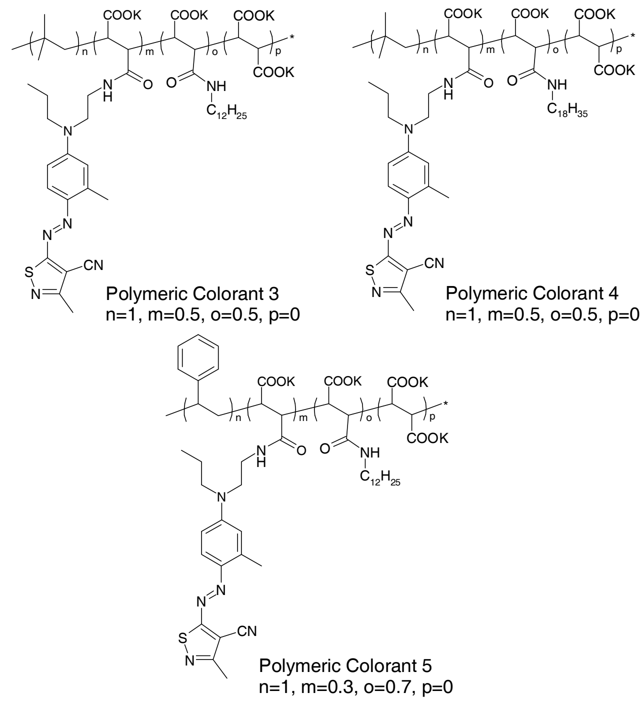
Receiver	Receiver description
Receiver 1	Great White MultiUse 20# Paper
Receiver 2	Xerox Premium Multipurpose 20# Paper, 92 Bright
Receiver 3	Hammermill Enhanced Multipurpose Office 20# Paper
Receiver 4	HP Multipurpose 20# Paper, 92 Bright
Receiver 5	OJI A4
Receiver 6	HP Advanced Multipurpose 20# Paper, 92 Bright
Receiver 7	Georgia Pacific IJ 24# Paper, 92 Bright
Receiver 8	Kodak Bright White IJ 24# Paper, 110+ Bright
Receiver 9	HP Color IJ 24# Paper, 100+ Bright
Receiver 10	Xerox Extra Bright IJ 24# Paper, 95 Bright
Receiver 11	Georgia Pacific IJ 24# Paper, 94 Bright,
Receiver 12	Staples IJ 24# Paper, 102 Bright

Optical Density on Plain Paper

Several inks were formulated with different polymeric colorants of the desired design at different concentrations listed in Table 3. These inks were printed on the 12 receivers described earlier in Table 2 and the optical density (Status A) at 100% dot coverage was measured with an X-Rite densitometer. The results are plotted in Figure 1 and reflect the versatility of these polymeric colorants in providing different optical density levels based on structure and concentration in ink, achieving levels of up to 1.3-1.4 that most pigment and dye inks have difficulty reaching.

Table 3. Concentration of polymeric colorants in printed inks

Inks	Polymeric colorant	Conc. of polymeric colorant in ink
Ink 1	Polymeric colorant 1	5%
Ink 2	Polymeric colorant 1	10%
Ink 3	Polymeric colorant 3	5%
Ink 4	Polymeric colorant 4	5%
Ink 5	Polymeric colorant 5	5%
Ink 6	Polymeric colorant 5	7.50%
Ink 7	Polymeric colorant 5	10%



***Scheme 3**. Structures of polymeric colorants in Table 3.*

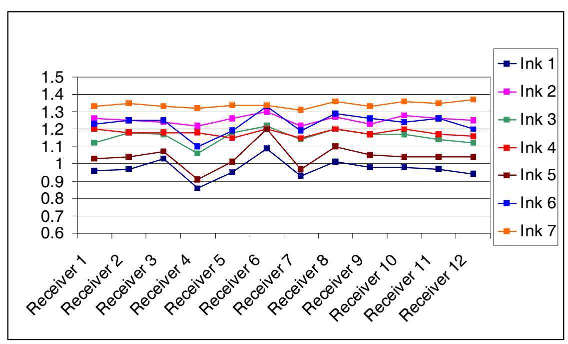


***Figure 1.** Optical density of polymeric colorants on plain paper receivers.*

Summary and Conclusions

Polymeric colorants were prepared from styrene maleic anyhydride copolymer and amine functionalized dyes for inkjet ink evaluation. Additive amines reacted with the polymeric colorants resulted in materials with modulated waterfastness as a modification of hydrophobicity. The additive group was found to be critical in attaining excellent waterfastness and optical density on bond papers.

Acknowledgments

The authors thank management of the Research Laboratories, Eastman Kodak Company, for support of this research and Dr. Douglas Bugner for his review of this manuscript.

References

[1] P. MacFaul, Ink Technologies for Inkjet Printing, Surface Coatings International, Part A, Issue 2004/10, pp. 420-426.

[2] J. Bishop, et al., "Inkjet Inks Containing Nanoparticles of Organic Pigments," U.S. Patent 5,679,138 issued 10/21/1997.

[3] S.F. Pond, Inkjet Technology and Product Development Strategies, Torrey Pines Research, 2000.

[4] A. Andrievsky, et al., "Inkjet Ink Compositions Containing Self-assembling Colorants and Printing Process," U.S. Patent 6,827,768 issued 12/07/2004.

[5] G.L. House, et al., "Pigment Nanoparticle Dispersions with Polymeric Dispersants for Aqueous Inkjet Inks," WO2006019662, issued 2/23/2006.

[6] SMA1000, Styrene Maleic Anhydride Copolymer, Sartomer Company Inc., Exton, PA, USA.

Author Biography

Mihaela Madaras completed her graduate education at the University of North Carolina at Chapel Hill, graduating with a Ph.D. in Organic Chemistry in 1997. Her postdoctoral work at Ohio State University between 1997 and 1999 involved the synthesis of a chromophore-modified DNA for ultrafast laser studies. She began work at Eastman Kodak Company in 1999 and has focused from the beginning on the synthesis, characterization, and formulation of new dyes and pigments for inkjet applications.