Improving the Performance Properties of Aqueous Based Ink-Jet Inks

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Abstract

With continued growth of aqueous pigmented inkjet ink into new, more demanding applications, there is an increasing need for aqueous ink jet systems with improved stability, color and adhesion/ durability on a range of substrates.

This paper describes some fundamental work on tailoring resins and additives for different end use applications and evaluates the potential for enhanced performance. The influence of various resin technologies on ink stability and jettability will be reviewed. Using the latest nano-mills, the effect of dispersion characteristics on final ink properties and stability will also be examined.

Introduction

Resins and polymeric dispersants (LZ hyperdispersants) have been utilized by the manufacturers of water-based inks and coatings for a variety of reasons, all associated with improvements in the performance of water-based inks for ink -jet printing. The benefits include:

- Enhanced flocculation resistance (dispersant)
- Reduction in milling time (dispersant)
- Improved viscosity control (dispersant)
- Superior color and gloss development (dispersant)
- Better adhesion on to substrates (resin)
- Improved water-resistance /wash-fastness (resin)

Polymer Dispersants

Polymeric dispersants can be described as having two key components in their structure, anchoring groups that adsorb on to the pigment surface and polymeric chains that provide a steric stabilization barrier around the pigment particle. Dispersants can be designed with single anchor - single chain or multi anchor – multi chain structures, and a variety of possible anchor chemistries. Polymeric chains should have good solubility in the continuous phase and maintain steric stability as the ink or coating cures. The key requirement of the anchor is to provide a strong attachment to the pigment or particle surface and that there is a sufficient density of coverage to minimize particle to particle interaction. Anchor groups have been developed for a wide variety of pigments and particles. Polymeric dispersants are not only utilized in the manufacture of pigment dispersions,
but also for pre-treatment of pigments during manufacturing to optimize dispersion.

Special Considerations in Inkjet

The key issue in optimum pigment dispersion is not just achieving acceptable particle size but also maintaining the target specification under a variety of formulation and storage conditions. Unless the pigment particles are fully and irreversibly stabilized, flocculation and aggregation are likely. This will lead to particle size growth, viscosity increase, settling and/or print head problems. The unique requirements of inkjet, namely ultra fine pigment dispersion and very low viscosities, means careful attention must be paid to the selection of dispersants and stabilizing additives. Indeed, while conventional polymer dispersants and additives commonly used in fluid inks and high performance coatings applications are often recommended for dispersions designed for digital inks. In reality as wide varieties of *inkjet grade* pigments are introduced the usual dispersant selection and dosage rules no longer seem to apply. Therefore, the opportunity and perhaps the need to develop optimized polymeric dispersants for inkjet exists.

Continuing developments in pigment technology and dispersion/milling equipment have made *nano-pigments* and *nano-dispersions* the first choice for pigmenting digital inks. Generally we consider these pigments/dispersions to have primary particle size < 200 nm and typically < 100 nm, which has required a rethinking of the dosage requirements for polymeric dispersants. In traditional fluid ink and coating applications, the rule has been to use 2 mg of active dispersant per meter^2 of pigment surface area (BET nitrogen absorption). In practice this is calculated by dividing surface area by 5, giving an AOWP (additive on weight of pigment) ranging from 2% for low surface area inorganic pigments to 80% for high surface area carbon blacks. As average particle sizes move below 100 nm and stabilization of the pigment dispersion becomes critical in very low viscosity inks at relatively low pigment percentages, the required dosage of polymeric dispersant has effectively doubled. For most dispersant/pigment combinations, the new starting point is 4 to 5 mg active dispersant per meter^2 of pigment surface area. There are two important points to be made regarding these new recommendations. First, the dispersants being evaluated are structurally very similar to, or in some cases identical to those used in high performance applications such as automotive refinish coatings or packaging inks where the same or very similar pigment types and solvents are encountered. Second, in the design of pigment concentrates for inkjet, the final ink viscosity requirements limit the variety and amounts of wetting/dispersing resins that can be used in the dispersion phase, and therefore, the dispersant must provide the bulk of the dispersion stability in the final ink. So while it would be expected that increased dispersant dosages would be required to stabilize dispersions of pigments optimized for inkjet with higher surface areas, the actual amount required appears to be even higher. Compared to traditional applications of polymeric dispersants where pigment concentration and stability in the mill base are equal in importance to the stability of the formulated ink or coating, the increased dosage of polymeric dispersant required in the mill base might limit the ultimate pigment concentration. However, that trade-off is required (and acknowledged) to achieve the required stability in the final ink. In practice, the pigment concentrations in the pigment concentrate are still 20-25% higher when using the optimal polymeric dispersant at the higher level compared with using only a dispersing resin, which will not provide the required stability in any case.

New Developments

High performance exterior durable pigments continue to replace metal complex dyes in variety of inkjet applications. This trend has increased the need for more effective polymeric dispersants in these inks. Since many of the exterior grade pigments selected for use in these wide format applications are familiar from other exterior applications, there is a basic understanding of the anchor chemistries that might be most effective for a given pigment. In practice, the traditional dispersants for these pigment types have performed adequately, especially at increased dosages. However, there is still much room for improvement in viscosity and particle size stability especially with certain key pigments. Modifications of traditional industry standard polymeric dispersants have shown improvements in addressing some of these concerns and new anchoring technologies have also shown promise for the development of dispersants optimized for ultrafine non-aqueous pigment dispersions.

One key in the evaluation of new dispersant candidates has been optimizing the milling process to ensure maximum particle size reduction. In general, a three stage process is used: pre-mix by high speed dispersion, grinding in a Dispermat® SL mill with 1.0 mm zirconium silicate to reduce particle size to < 300 nm, and then the final grind on a nano-mill like DYNO®-MILL RL (WAB AG) with 0.1/0.05 mm yttrium stabilized zirconia media. Early results indicate that the degree of dispersion in the nano mill is an important indicator of the ultimate viscosity and particle size stability in the final ink. Determining the actual *end point* of the dispersion is an ongoing effort. The theory being considered is that it is vital to treat the highest percentage of primary particles completely as possible since the higher the concentration of aggregates, or undertreated particles remaining, the more likely there will be flocculation (agglomeration) or particle size growth in the final ink. Reasons this might be more important in nano dispersion milling than in traditional media milling include the significantly increased pigment surface area, stronger inter particle forces, and the impact of solvents and resin/binder in the final ink that could wet out unstabilized surfaces or agglomerates. More than ever, the strength of adsorption of the anchor groups on the pigment surface is critical to final performance.

Evaluation of nano-pigment dispersions and the resulting formulated inks is straight forward, with the stability tests (viscosity and particle size) being performed at 25 °C and 70 °C over a period of weeks. Viscosity is measured using a AR1000 Rheometer (TA Instruments). Particle size is characterized using a Zetasizer (Malvern Instrument.) utilizing dynamic light scattering. A typical study investigating a new dispersant technology examined the stability of an inkjet grade magenta (CI Pigment R-122) dispersed with our polymeric dispersant and a solvent for use in a wide format water-based ink. Performance of the new technology dispersant was compared to a modified version of a current technology dispersant known to perform well with this pigment type. Milling trials established the proper parameters to achieve the ultimate particle size reduction and dispersant dosage (AOWP, additive on weight of pigment) was varied to determine the dispersion and ink stability as measured by particle size distribution after weeks aging at 70 °C. The average particle size specified by the pigment manufacturer is 95 nm. The results are shown in the table below.

Dispersant	AOWP	D50(nm)	D90 (nm)
Conventional	50%	320	540
Developmental	50%	170	340
Developmental	80%	120	240

For this inkjet grade magenta, it is clear that the new dispersant technology provides superior dispersion stability, clearly outperforming the standard recommendation, even at the increased dosage. The combination of an optimized anchor and the increased dose is vital to achieving the best stability.

Water-based Resins for Ink-Jet Inks

Several resins for water-based inks are available in the market. Most important parameters for the selection of proper resins are particle size of these dispersion and the viscosity at dilute concentrations. Several water-based resins were screened for water-based ink jet inks for printing on different substrates such as photographic papers, textiles and other non-porous substrates (PVS, PP, PE etc.). The resins were tested for printing on uncoated and coated substrates using water-based ink- jet inks. The ink were made with various pigment dispersions available in the market and also made with our own water-based hyperdispersants for comparison.

The dispersions were mixed with the test resins one at a time and tested for its bulk properties such as viscosity and surface tension at 3 wt% concentration to a test formulation. Once passed these requirements for jetting in an ink jet printers, inks were drawn on to various substrates such as photographic papers (HP, Epson) as well as several coated and uncoated vinyl substrates. The inks were prepared according to the formulation above and applied to the given substrates with a #4 WWR and dried at 60° C for 1 minute prior to testing. Dry rub was tested by simply rubbing a finger over the surface and noting how difficult it is to remove the film. Scratch Resistance is tested with the back of the fingernail. Tape adhesion was run by smoothing the 3M 610 tape over the ink surface and removing slowly in a 180° Peel. The percent of ink that remains adhered to the film is estimated. Viscosity is measured on a TA plate and cone viscometer for the inks made for the testing. The shear rate sweep from 10 to 300 sec^{-1} produces a Newtonian curve where the viscosity is determined by the slope of the shear stress vs. shear rate line. Viscosities of the inks are all around 2-4 cps range suitable for jetting with Epson type printers.

Testing in the printers was done initially using Epson 88 plus desk top printers that was modified for ease of use. Cyan, Magenta, Yellow and Black inks were made with the experimental dispersion and resins and tested for primeability of the printer, printer performance, and start up from idle from 24 hrs and 48 hrs to understand the recovery time. Inks that passed the test were tested again using an Epson 7800 wide format printer that can print up to 24" wide for long for printer performance while printing wider prints. This printer will be closely simulated to wide format printers like Mimaki or Rolland printer with Epson printheads.

The inks performed well but the color saturations are different from the type of dispersion used and the resin used in each test . Based on the test results tabulated in Tables 1-4 we conclude that some of our experimental resins like R1007-OS and R-1001-OS out perform the OEM inks used in the market for similar applications. Also, PUD emulsion used in this study out performs any of the acrylic emulsion currently being used in the market. We have classified these resins and hyperdispersants as top performers exclusively for ink-jet printing market.

TABLE 1 &2 : Performance of Select Binder Resins on Several Vinyl subst Films

Polymer	ORAJET Dry Rub/Scratch Resistance		ORAJET Adhesion
R-1007-OS	Good	Good	100%
R-1001-OS	Poor	Poor	5%
R-331-OS	Poor	Poor	0%
R-514-OS	Poor	Poor	95%
Control	Poor	Poor	75%

Polymer	AVERY Dry Rub/Scratch Resistance		AVERY Adhesion
R-1007-OS	Good	Good	100%
R-1001-OS	Poor	Poor	0%
R-331-OS	Good	Good	100%
R-514-OS	Fair	Poor	90%
Control	Poor	Poor	0%

TABLE 3: Formulated Coatings on untreated Orajet vinyl

	Dry Rub	Adhesion
Control	Fair	70%
R-1007-OS	Good	100%
833-09-053	Fair Poor wet out	100%
R-1007-OSF	Good	100%
833-09-053	Poor wet out	—

Future Work

A variety of important ink jet grade pigments are being studied using modified conventional technology and developmental dispersants in resin free water-based pigment dispersions. These dispersions are being evaluated in a broad range of resin containing inkjet inks. Preliminary results indicate that promising new technology dispersants provide the best stability across a range of important pigments. The concept of optimizing dosage is also being validated not only based on pigment surface area but also with particle size. With the help of new resin chemistries available adhesion on to different substrate can be attained for printing onto much wider substrates.

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Biography (Presenting Author)

Deverakonda Sarma has 20 years experience in Ink-Jet and Electro-photography technologies including ink/toner formulations, colorants, pigment dispersion and rinter platforms. He has been with Lubrizol Advanced Materials Inc. in Brecksville, OH for the past two years. He is currently Global Applications Manager for Graphic Arts, focused on providing product and technical support for Lubrizol's digital customers. He also works closely with the market development activities in the Americas for all digital ink applications.