Developments in Dispersants for Inkjet

Jeff Norris; Lubrizol Advanced Materials; Brecksville, OH

Abstract

With the continued growth in pigmented inkjet, particularly for wide format applications, the development of new additives is critical to the formulator's ability to meet future requirements on ink stability, faster print speeds and enhanced print quality. In particular, the continuing development and use of nano sized pigments to reach a wider color gamut requires an increasing dependence on dispersants to achieve stable formulations.

Fundamental work on tailoring dispersants for different pigments in solvent and UV cured formulations has shown the potential for enhanced performance. Using nano mills, the efficiency of different dispersant technologies can be compared to optimize both millbase and ink storage stability in terms of viscosity and particle size. As is expected, the dispersant dosage becomes more critical as particle size is decreased and ongoing studies could yield better predictive rules for formulating nano-pigmented inks.

Pigment Dispersion and Stabilization

Polymeric dispersants (hyperdispersants) have been utilized by the manufacturers of inks and coatings for a variety of reasons, all associated with improvements in the state of pigment dispersion. The benefits include:

Productivity
- High pigment loading without increased viscosity
- Reduction in milling time
- The manufacture of millbases with broad compatibility

Quality
- Improved viscosity control
- Superior color development

Stability
- Enhanced flocculation resistance

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 chemistry is that a strong attachment to the pigment or particle surface is achieved and that there is a sufficient density of coverage to minimize particle to particle interaction.[1] 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 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 increasing 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 dispersants for inkjet exists.

Continuing developments in pigment technology and dispersion/milling equipment have made *nanopigments* and *nanodispersions* 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 66% 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 millbase are equal in importance to the stability of the formulated ink or coating, the increased dosage of polymeric dispersant required in the millbase 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 solvent based and UV cured wide format 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 and with solvents and monomer/oligomers that are increasingly used to improve adhesion to low energy substrates. 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 nonaqueous 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 (BYK-Gardner) with 1.0 mm zirconium silicate to reduce particle size to < 300 nm, and then the final grind on a DYNO®-MILL RL (WAB AG) with 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 *endpoint* 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 aggressive solvents and monomers 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 nanopigment dispersions and the resulting formulated inks is straight forward, with the stability tests (viscosity and particle size) being performed at 25 °C and 50 °C over a period of weeks. Viscosity is measured using a Bohlin Visco 88 cone & plate viscometer (Malvern Instruments Ltd.). Particle size is characterized using a NanoTrac NPA250 (Microtrac Inc.) 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 only polymeric dispersant and solvent (ethylene glycol butyl ether acetate) for use in a wide format solvent 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 two weeks aging at 50 °C. The average particle size specified by the pigment manufacturer is 95 nm. The results are shown in Table 1.

Dispersant	AOWP	D50 (nm)	D90 (nm)
Conventional	80%	321	890
Developmental	50%	67	117
Developmental	80%	47	76

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.

Future Work

A variety of important pigments are being studied using modified conventional technology and developmental dispersants in resin-free solvent based and monomer based pigment concentrates. These dispersions are being evaluated in a broad range of model solvent based and UV cured inkjet systems. Preliminary results indicate that promising new technology dispersants provide the best stability across a range of important pigments. The concept of increased dosage is also being validated not only based on pigment surface area but also with particle size.

Acknowledgements

The author would like to thank to Dr. Ian Maxwell, David Cartridge, Greg Brown, and Lee Moreland for their assistance in preparing this paper and the related conference poster presentation.

References

[1] J. D. Schofield, Handbook of Coatings Additives Vol. 2, (Marcel Dekker; NY, 1992), Chapter 3.

Author Biography

Jeff Norris has 25 years experience in colorants, pigment dispersion and dispersant technology, the past nine years with Lubrizol Advanced Materials, Inc. in Brecksville, OH. He is currently Technical Market Manager for Graphic Arts and Functional Coatings, focused on providing technical and commercial support for Lubrizol's hyperdispersant, surface modifier and specialty polymer product lines. He also coordinates technical service and market development activities in the Americas for digital ink and radiation cured applications.