

# Polymer Stabilized Pigment Dispersions for High Reliability Ink-Jet Printing

Tom Annable, Owen Lozman and Paul Ewing; Fujifilm Imaging Colorants; Manchester, UK.

## Abstract

*Due to their excellent water and fade resistance properties and their low environmental impact, aqueous pigment dispersions are of growing importance in emerging high throughput aqueous ink jet markets. However, the physical durability (abrasion resistance) of pigment-based inks is often poor. In this paper we describe how dispersing pigments with polymeric dispersants enables significant advantages in abrasion resistance, whilst also delivering stable dispersions across the wide range of ink formulations required to print reliably at high speed, and rapid coagulation on a wide range of substrates. We show that to achieve stability it is essential to irreversibly anchor the dispersant to the pigment surface, and then provide the appropriate balance of electrostatic and steric inter-particle interaction in order to prevent particle aggregation in the ink. We show how these challenges can be met with a new type of pigment dispersion based on Reactive Dispersant technology.*

## Ink-Jet Ink Design

An ink-jet ink for high throughput applications has to deliver performance in three basic areas:

1. Reliable jetting from the nozzle: To generate reproducible ink droplets without satellites nor a significant ligament or tail – particularly important for single pass printing.
2. Controlled ink behavior on the substrate: To minimize penetration/bleed & migration processes while the ink is still mobile.
3. Satisfactory final image properties on the substrate.

In high throughput printing applications, the requirement to print uninterruptedly at high speed places particular emphasis on tailoring the ink chemistry to deliver high reliability. One key aspect of ink performance that underpins high reliability is open time – the period of time that ink can reside (without jetting) in an uncapped nozzle before jet failure occurs. Broadly speaking, the longer the open time, the more suited the ink class is to high operability single pass ink jet applications.

Aqueous inks provide a particular challenge in achieving high open-times due to the volatility of the continuous phase and the various property changes that can occur during the evaporation process. Some of the changes that may occur are:

1. Viscosity increase.
2. Surface tension change.
3. Phase change (eg. from polymeric components or in the cosolvent mixture).

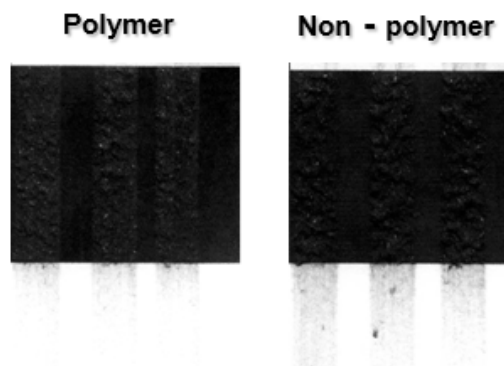
4. Precipitation (of pigment or polymer components).
5. Aggregation of pigments.

In designing an aqueous ink for improved open-time, several strategies can (and are) employed. The first is to increase the humectancy of the ink such that the time to reach the critical viscosity is longer than the target open-time. The second approach is to decrease the amounts of the most volatile solvent (typically water) and to increase the content of lower volatility solvents (ie. to increase the organic solvent content in the ink).

In order to deliver the ink behavior on the substrate and the required final image properties, it is essential to select the appropriate colorant technology. Due to their superior lightfastness, bleed control, optical density and wetfastness on the substrate, pigments are often the choice of colorant for the ink development chemist. However, the appropriate choice of pigment dispersion technology is key to the success of the formulator in meeting the ink design challenges. In the following sections, we consider the choices of pigment technology and their strengths and weaknesses in delivering the three basic performance requirements.

## Targets for Pigment Dispersing Technologies

In developing a pigment dispersion technology, it is, of course, a fundamental requirement that the technology provides successful stabilization in the ink over its lifetime and during the conditions of use. This is only a minimum requirement. The pigment dispersion technology must also provide a controllable coagulation rate (and so penetration and optical density) and a robust film on the substrate.



**Figure 1:** Demonstration of the wet-rub resistance of a print (on plain-paper) produced with a polymer (Reactive Dispersant technology) stabilized dispersion and a non-polymer stabilized dispersion (functionalized pigment).

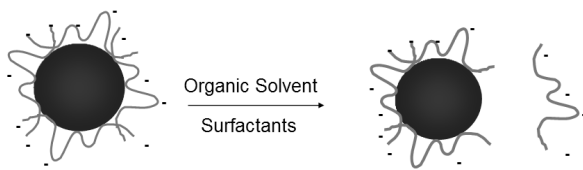
The benefits of polymer stabilization are clear from Figure 1 which illustrates the web-rub resistance of prints. The polymeric dispersant provides vastly superior rub resistance (in fact, in this case, any visible transfer arises due to paper damage rather than failure of the ink film). So, it is best to choose polymeric dispersants as these provide the necessary particle binding within the ink film. This allows the formulator to develop inks with good on-substrate performance. However, as will be shown below, the production of dispersions with polymeric dispersants requires some attention to their design in order to develop the requisite stability in the ink.

## Stabilization of Pigment Dispersions

The effectiveness of a dispersion technology for stabilizing pigments in high organic content inks depends on achieving two main requirements:

### 1. Anchoring of the dispersing species.

It is essential that the stabilizing chains or groups are irreversibly anchored to the surface of the pigment dispersion in order that the pigment is not destabilized by desorption of the dispersant. This is illustrated in Figure 1.



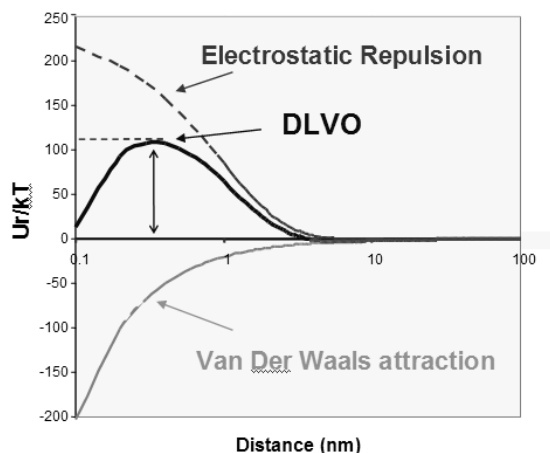
**Figure 1:** Failure of dispersant anchoring in a dispersion.

### 2. Stabilization via interparticle repulsion

In order to overcome the strong, short-range Van der Waals attraction between colloidal particles, it is necessary to have a mechanism of interparticle repulsion. In aqueous systems, two main classes of stabilization are possible:

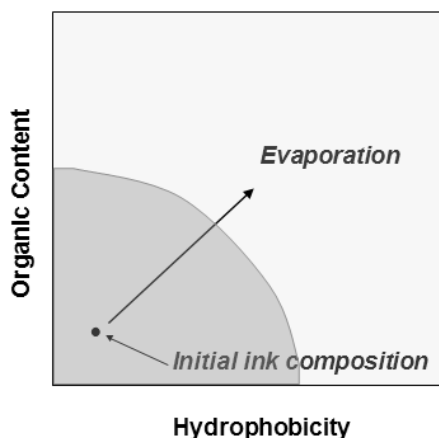
1. Electrostatic – anchoring of charged groups onto the particle surface
2. Steric – anchoring of polymer chains onto the surface

In polymer stabilized dispersions, a combination of both mechanisms is often used (electrosteric stabilization). The DLVO theory of electrostatic repulsion is illustrated in Figure 2. This theory accounts for the combined effects of inter-particle attraction through Van Der Waals interactions and repulsion through electrostatic interactions.



**Figure 2:** DLVO theory of electrostatic repulsion illustrating the net interparticle repulsion as a function of inter-particle separation (nm).

Achievement of both anchoring and inter-particle repulsion is particularly challenging in applications demanding high open-time inks due to their high initial organic solvent content and since the evaporation of water from the inkjet nozzle will result in a further increase in the hydrophobicity and organic content of the ink within the printhead. This is illustrated in the schematic diagram in Figure 3.



**Figure 3:** Illustration of the compositional changes occurring as an ink evaporates. The shaded area shows the stable region for the pigment dispersion in the ink.

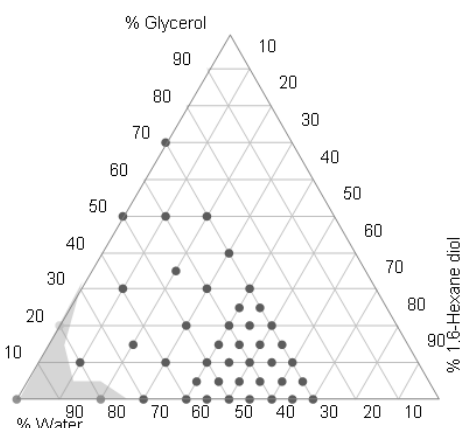
During evaporation, the ink becomes progressively more hydrophobic and higher in organic content (assuming lower volatile organic solvents are used) thus weakening the adsorption of the dispersant on the pigment surface. At some point, the pigment dispersion may become unstable due to the desorption of the dispersant or, due to the decreasing dielectric constant of the vehicle, reduction in the interparticle repulsion arising from the surface charge.

The larger the stability window, the greater the formulation flexibility of the dispersions and the more suitable for use in high open-time aqueous inks. Of course, it is highly undesirable to formulate inks in close proximity to the boundary between the stable and unstable regions. From the point of view of dispersion selection it is advisable to choose a dispersion technology which maximized the stable region in order to have the maximum opportunity for optimizing the ink for print-head operability as well as for on-substrate performance.

## Dispersion Technologies

There are several methods to stabilize pigment dispersions for use in ink-jet inks. We will illustrate the stability of each of the main dispersion technologies in turn in the following sections. The assessment of stability was performed by creating ternary mixtures of 1,6-hexanediol, glycerol and water with the dispersion at a typical concentration used in inks. The stability was assessed by optical microscopy after 1 week at 25°C. The dispersion was deemed to be unstable if there were any visible signs of aggregation.

### 1. Surfactant Stabilized Dispersions.



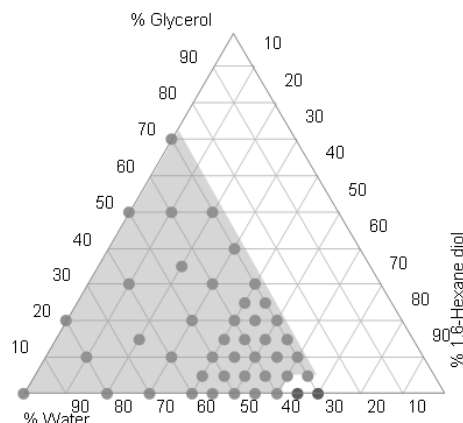
**Figure 4:** Phase diagram for a low molecular weight dispersant stabilized dispersion. The shaded region represents the stable region. The dots show the compositions measured (due to the water content in the pigment dispersion, not all of the compositional space could be accessed).

The stability of an anionic low-molecular weight surfactant stabilized dispersion is shown in Figure 4. Increasing the hexanediol concentration in the mixture or decreasing the water content has a dramatic effect on the stability of the dispersion. In this case, although the surface charge is high, the dispersant anchoring is poor.

### 2. Polymer Stabilized Dispersions

The stability of an optimized anionic high-molecular weight polymeric dispersant stabilized dispersion is shown in Figure 5. The dispersion is stabilized to a much higher degree than apparent

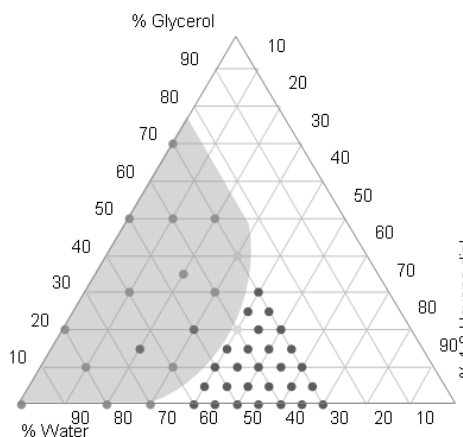
for the surfactant system, although there is failure evident at high 1,6-hexanediol concentrations. In this case, the surface charge is high and although the dispersant anchoring is much improved there are still signs of anchoring failure in the most hexanediol rich ink vehicles.



**Figure 5:** Phase diagram for a dispersion stabilized with an optimised high molecular weight polymeric dispersant. The shaded region represents the stable region.

### 3. Functionalized Dispersions

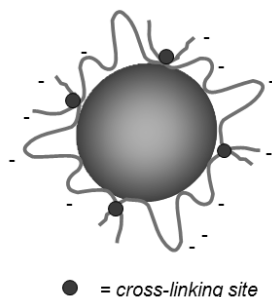
The stability of a functionalized pigment (ex Cabot Corporation) in ternary mixtures of water, glycerol and 1,6-hexane-diol is shown in Figure 6. In this case, the dispersion has insufficient surface charge or steric stabilisation to be stable across all regions of the ternary phase diagram despite the covalent attachment of the stabilizing groups.



**Figure 6:** Phase diagram for a functionalized pigment with covalently attached charged groups. The shaded region represents the stable region.

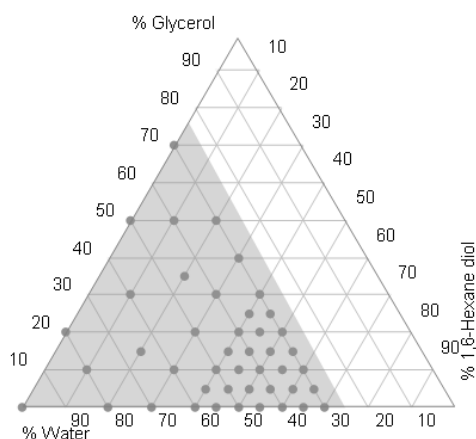
#### 4. Reactive Dispersant Stabilized Dispersions

Reactive Dispersant technology addresses many of the issues of stabilization of colloidal dispersions. This has several advantages over the previous dispersion technologies in that it allows the benefits of polymer based stabilization technology, in particular its excellent durability, without the drawback of poor dispersant anchoring. The principle is illustrated in Figure 7.



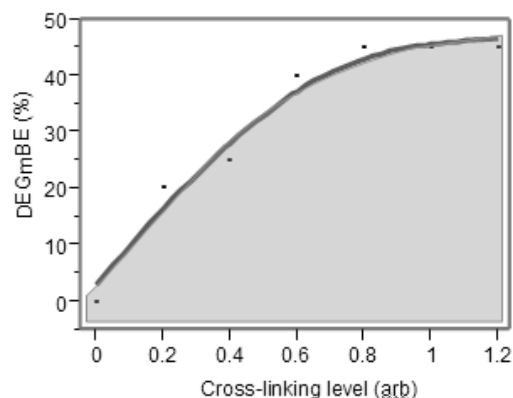
**Figure 7:** A schematic illustration of Reactive Dispersant Technology.

In order to eliminate dispersant desorption, the adsorbed polymeric dispersant is cross-linked on the pigment surface. This approach is considerably more versatile and pigment surface independent than the alternative approach of bonding of the dispersant via covalent reaction to the surface.



**Figure 8:** Phase diagram for a cross-linked polymeric dispersant (Reactive Dispersant). The shaded region represents the stable region.

The stability of a Reactive Dispersant based dispersion is shown in Figure 8. The dispersion is stable across the entire ink tested region illustrating that it delivers firm anchoring as well as providing a high inter-particle repulsion. The use of reactive dispersant technology allows more flexibility in the polymer design as many dispersants are optimized on the basis of the need for better anchoring, rather than, for example, on-substrate performance.



**Figure 9:** The maximum tolerable amount of diethylene glycol mono butylether before there is observable aggregation of a polymeric dispersant based pigment dispersion in which the dispersant is cross-linked to varying extents (arbitrary units). The shaded area illustrates the stable region.

To illustrate the benefits of the cross-linking process in more challenging inks, Figure 9 shows the resistance to diethylene glycol mono butylether. As the cross-linking level is increased, the tolerance to the water-miscible but relatively hydrophobic cosolvent is enhanced. At high cross-linking levels, the dispersant desorption is prevented. In order to achieve stability at even higher solvent levels, it is possible, without compromising the dispersant anchoring, to adjust the dispersant charge or steric stabilization to ensure compatibility in the target ink vehicle.

#### Conclusions

The design of high throughput inkjet inks with suitable on-substrate performance can be achieved through the use of Reactive Dispersant technology. Such technology allows the enhanced physical durability achievable with polymer-stabilized dispersions but without the poor stability performance that can limit their use. Cross-linking of the dispersant around the pigment surface eliminates loss of anchoring which is the predominant failure mode in conventional polymer based dispersions. Solving this problem, means that cross-linked polymer based dispersions can be optimized through tailoring of the dispersant structure for on-substrate performance and reliable jetting performance rather than for dispersion stability.

#### Author Biography

Tom Annable received his BSc in chemistry from Heriot-Watt University (1986) and his PhD in polymer physical chemistry from Lancaster University (1989). He joined ICI Colloid Science Group (1989), NeoResins (1994) before joining the ink-jet business, now a part of Fujifilm (2003). His work has focused on the development of polymer and pigment dispersion technology for aqueous ink-jet applications.