Ink Systems for the Xaar Ink Jet Printhead

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Abstract

Advantages of the oil-based pigmentary inks in the Xaar printhead[1,2], when compared with conventional water-based ink jet inks, include high lightfastness, absence of cockle on paper substrates and a rapid dry time which facilitates higher printing speeds. This paper will first describe the mechanisms for achieving the required colloidal stability of the finely divided pigment particles. The colour gamut accessible using a trichromatic ink system is to some extent dependent upon the lightfastness required. The compromises involved will be discussed, and reference made to the availability of certain high chroma pigments that are only suitable for use in non-aqueous ink systems. Enhancement of the colour gamut, particularly in the secondary colour regions, by application of a six ink set will then be discussed. Finally, the capability of the Xaar printhead to jet UV cure inks, and the benefit of such inks in terms of durability on non-porous substrates such as film, metal and glass will be disclosed.

Introduction

The use of oil-based inks in the Xaar piezo printhead brings a variety of benefits including:

- Rapid drying time permitting high printing speeds
- Absence of cockle on paper substrates
- High lightfastness through correct pigment selection

Successful manufacture of these inks requires a very high level of dispersion stability, and the mechanism required to give colloidal stability in the non-polar oil media (which is actually similar to that used in lithographic printing) is very different from that required in aqueous pigmentary ink jet systems.

The use of coloured (as opposed to black) pigmentary inks in aqueous or oil-based drop-on-demand ink jet is a relatively new development. The significant differences seen in colour space values for cyan, yellow and magenta inks from different suppliers show that pigment dispersion systems, and even pigment selection, have not yet reached the development stage achieved by dye-based ink systems, and that further improvements should be anticipated. A rational choice of pigments should either maximise chroma or maximise lightfastness. This paper attempts to outline the options available in such systems, and suggests optimum ways of increasing the number of colours in the IJ printing system as a further route to enhancing the available colour gamut.

Piezo ink jet printheads also permit the firing of inks that do not have a volatile component, a feature of particular benefit for the printing of 100% solids UV cure inks. Inks of this type, suitable for firing in a Xaar type IJ printhead have now reached the demonstration stage, and show much promise.

The Stabilisation of Pigment Dispersions in Oil-based IJ Inks

Because of the relatively low dielectric constant of all the common organic solvents, the electrostatic stabilisation mechanism (as commonly used in aqueous colloidal dispersions) is not effective. Instead we must rely upon the so called "steric stabilisation" mechanism. This type of stabilisation is generated via the absorption of a layer of surfactant, resin or polymer on to the surface of the pigment particle[3]. When two particles approach each other, and the layers of adsorbed material start to overlap, they effectively repel each other. This is illustrated very simplistically in Figure 1.
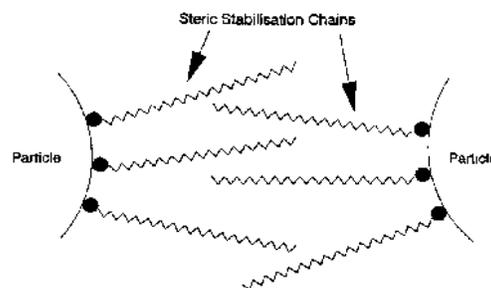

Figure 1. The Basic Steric Stabilisation Mechanism

Steric stabilisation can only occur when the polymer chains are very soluble in the continuous phase (i.e. the oil in an oil-based ink). In polymer solution theory terms, "better than Theta Solvent Conditions" are required.

Polymeric Hyperdispersants

A polymeric hyperdispersant contains two key structural features, namely a polymeric chain giving steric stabilisation in the desired continuous phase, and an anchor group capable of being strongly adsorbed on to the pigment particle surface. The polymeric chain must be matched in solubility terms with the continuous phase, and must be sufficiently long to create a steric barrier thick enough to overcome particle-particle interaction forces. The anchor group (which may be a functional group, or a different polymer block) must be matched with the surface of the pigment particle.

When a pigment has relatively reactive or ionic surface, as is the case with inorganic pigments or organic pigments that are chemically in a salt form, it is possible to form an ion-pair bond between a charged site on the particle surface and an oppositely charged functional group on the hyperdispersant. This mechanism is illustrated in Figure 2, the ion-pair bonding being particularly strong in this situation because of the low dielectric constant of the continuous phase.
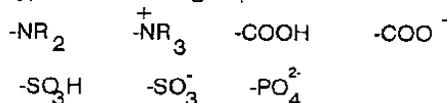

Typical functional groups:

$-NR_2$ $-\overset{+}{N}R_3$ $-COOH$ $-COO^-$

$-SO_3H$ $-SO_3^-$ $-PO_4^{2-}$

Figure 2. Anchoring via a Simple Ion-pair Bond.

Most organic pigments do not have charged sites on their surface, but they may contain hydrogen bond donor or acceptor groups such as esters, ketones, ethers or amides. It is then possible to form multiple relatively weak hydrogen bonds between the pigment particle surface and a suitably chosen polymer block. This arrangement is illustrated in Figure 3. It should be noted that the polymeric hyperdispersant is a "comb type" block copolymer.

Typical anchor groups:
Polyamines, Polyols, Polyethers

Figure 3. Anchoring via a Hydrogen Bonding Mechanism

Some organic pigments are not very responsive to either of the above mechanisms, and are normally considered to be relatively difficult to disperse. The chemical structure of the organic pigment itself may then be modified to act as an intermediary anchor group, or synergist. Because of the close structural similarity, the synergist molecule can pack very closely on to the pigment particle surface, and maximise the Van der Waals attractive forces between it and the pigment particle. In this mechanism, which is illustrated in Figure 4, the synergist is normally a charged derivative of the pigment. Through its adsorption on to the pigment particle surface, the synergist generates charged sites, and these charged sites then anchor a polymeric hyperdispersant via the same basic mechanism that was shown in Figure 2.
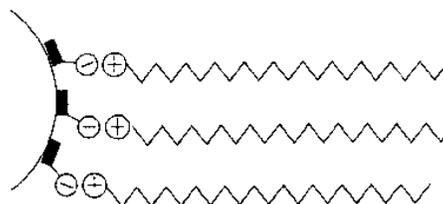
Typical synergists:
Modified copper phthalocyanine, by addition of polymeric chains, ionic, or substituted ionic groups

Figure 4. Anchoring via a Synergist

Pigment Options in Oil-based IJ Inks

The coloured pigments used so far in DOD aqueous ink jet have, to the best of the author's knowledge, all been covalently-bonded organic molecules (e.g. quinacridones, monoazos). The only exception is copper phthalocyanine, and in this particular molecule the copper atom is so strongly complexed that it can survive even strongly acidic conditions. There is, however, a further broad class of organic pigments - Lake Pigments - which are commonly used in the conventional printing industry, and have been known for many years. These are manufactured by taking a conventional bright water-soluble dyestuff, and precipitating it out of aqueous solution with an appropriate multivalent counterion. In the case of sulphonated direct dyesuffs, a divalent or trivalent metal is used - calcium is the most common because of the high insolubility of its salts, and because of its benign toxicological profile. The structure in Figure 5 is that of a typical such pigment, Pigment Red 52:1.
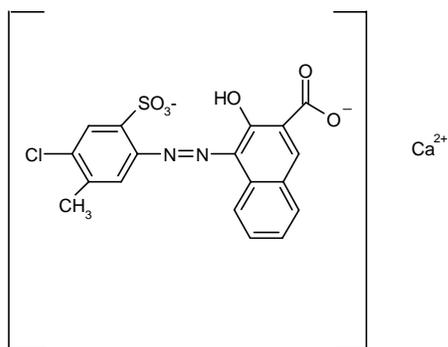
Figure 5. Pigment Red 52:1. A typical Calcium Lake pigment.

Basic or cationic dyestuffs (e.g. Rhodamines) are commonly laked with complex inorganic acids such as phosphotungstomolybdic acid (PTMA) or silicomolybdic acid (SMA). The structure In Figure 6 is that of a typical such pigment, Pigment Violet 1.
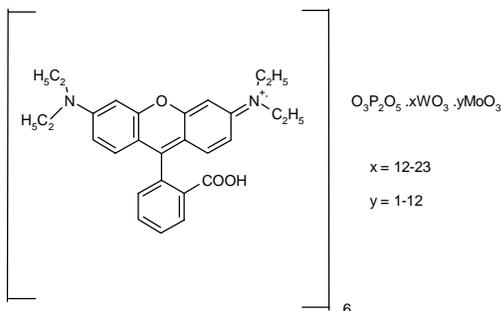

Figure 6. Pigment Violet 1. A typical Rhodamine based PTMA Lake Pigment.

The laking process does, in fact, tend to improve the lightfastness over that of the original basic dye, without destroying its intrinsically high chroma. The process for the manufacture of these pigments is rather difficult to control, and frequently results in a slight excess of one of the two main components.   Thus aqueous inks based on these pigments are often rather unstable, with the basic component interacting with the acrylic resins and precipitating out. Some "aqueous compatible" grades are believed to be under development, but it is by no means clear that they will be suitable for the extremely rigorous requirements of IJ printing inks. These problems do not present themselves in oil-based inks, and lake pigments are therefore ideal for the manufacture of bright pigmentary inks with chroma and lightfastness very similar to conventional dye-based inks.

Potential options for Ink sets using the Xaar Printhead

The demand for a very highlightfast IJ ink system has meant that the initial Xaar ink systems are based on a trichromat of very highlightfast pigments, giving virtually automotive paint lightfastness. The colour space chart in Figure 7 is that from such a set of pigments. It will be seen that Chroma

values are only slightly lower than those achieved with dye-based inks of much inferior lightfastness.
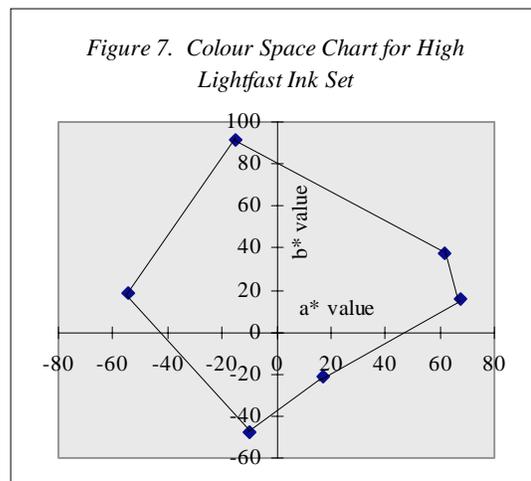

Figure 7. Colour Space Chart for High Lightfast Ink Set

Table 1 lists the types of pigments that may be used to generate a high lightfast Xaar IJ ink set.

Table 1. Pigment options for a trichromatic, high lightfast, IJ ink set.

COLOUR	PIGMENT TYPE
Cyan	Copper Phthalocyanine
Yellow	Monoazo or Isoindoline
Magenta	Quinacridone or Dimethylquinacridone

If, however, chroma is at a premium - the application may be an indoor display, or short duration, high impact outdoor signage - then the alternative trichromatic ink set shown in Table 2 could be envisaged.   Figure 8 is an example of the colour space available from one such ink set.

Table 2. Pigment options for a trichromatic, high chroma, IJ ink set.

COLOUR	PIGMENT TYPE
Cyan	Copper Phthalocyanine
Yellow	Disazo, Monoazo or Isoindoline
Magenta	Calcium Lake or PTMA Lake

Figure 8. Colour Space Chart for High Chroma Ink Set
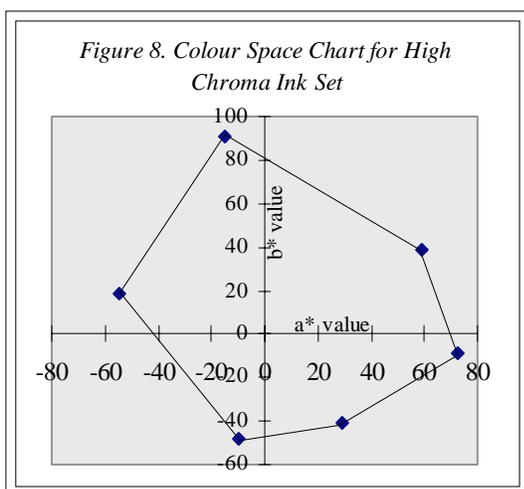
Increasing the number of inks in the IJ printing system is then a further route to enhancing the available colour gamut. (It should be noted that traditional textile printing has always used a large number of inks to maximise colour gamut.) IJ printer manufacturers appear to be opting for a six ink system (5 colours plus black), perhaps because this can be done by simply doubling the number of colour heads on the printer. Having opted for an increased number of inks, it is important that a rational choice of pigments should be made, maximising either lightfastness or chroma. Clearly, many of the options are still speculative, and precise colour space values will be dependent upon the effectiveness of the colloidal stabilisation mechanisms that can be used. Table 3 lists the author's view of some of the pigment types that should be considered for a high lightfast, 5 colour, IJ ink set.

Figure 3. Pigment options for a 5 colour, high lightfast, IJ ink set.

COLOUR	PIGMENT TYPE
Cyan	Copper Phthalocyanine
Green	Halogenated Copper Phthalocyanine
Yellow	Monoazo or Isoindoline
Red	Condensed Disazo or Naphthanilide
Magenta	Quinacridone or Dimethylquinacridone

The remaining deficiency in such a set is that of chroma in the violet/blue shade area, and any solution will probably require the addition of a further printhead.

For a high chroma, 5 colour IJ ink set, the pigment options for oil-based inks using Xaar printhead technology are much greater, because of the range of lake pigments available. Table 4 again lists the author's view some of the pigment types that should be considered.

Figure 4. Pigment Options for a 5 colour, high chroma, IJ ink set.

| COLOUR	PIGMENT TYPE
Cyan	Copper Phthalocyanine
Green	Halogenated Copper Phthalocyanine
Yellow	Disazo, Monoazo or Isoindoline
Red	Calcium Lake
Magenta/ Violet	Calcium Lake or PTMA Lake

In this set, the broad range of Lake pigments available allows one to select a bright pigment at the very violet end of the magenta range, thus enhancing chroma in the violet/blue shade area without significant loss of chroma in the magenta/red shade area.

The IJ Printing of UV cure inks

A potential benefit of any piezo IJ printhead, versus a thermal IJ printhead, is the possibility of firing inks that do not have a volatile component. This feature is of particular benefit for the printing of 100% solids UV cure inks. The use of UV cure inks permits the printing of very durable images on to non-absorbent substrates, and it is therefore clearly beneficial in such systems to use the UV cure resins in association with high lightfast pigments.

The 100% solids UV cure inks suitable for piezo IJ printing must have significantly lower viscosities than conventional UV cure inks. A high level of reactive diluent is needed to give the desired viscosity. This requires appropriate selection of prepolymer and multifunctional diluents to ensure that the final ink film has the desired adhesion and durability. The big difference in ink polarity versus an oil-based piezo IJ ink also means that a radically different steric stabilisation polymer chain must be used in the pigment dispersion system. Finally, the problems of curing in the presence of colourant (particularly carbon black, with its absorption of radiation over a broad wavelength spectrum) further increase the difficulties.

We have now developed a series of prototype UV cure IJ inks suitable for use in a Xaar printhead. These inks of been successfully printed on to a range of substrates including Polyester, HDPE, PP, PVC, ABS, tracing paper and glass. Figure 9 is an enlarged image of a print, and shows the definition that can be obtained with a 360 d.p.i. Xaar printhead when printing one of these prototype inks.

OUTSIDE BORDER289x577

50%
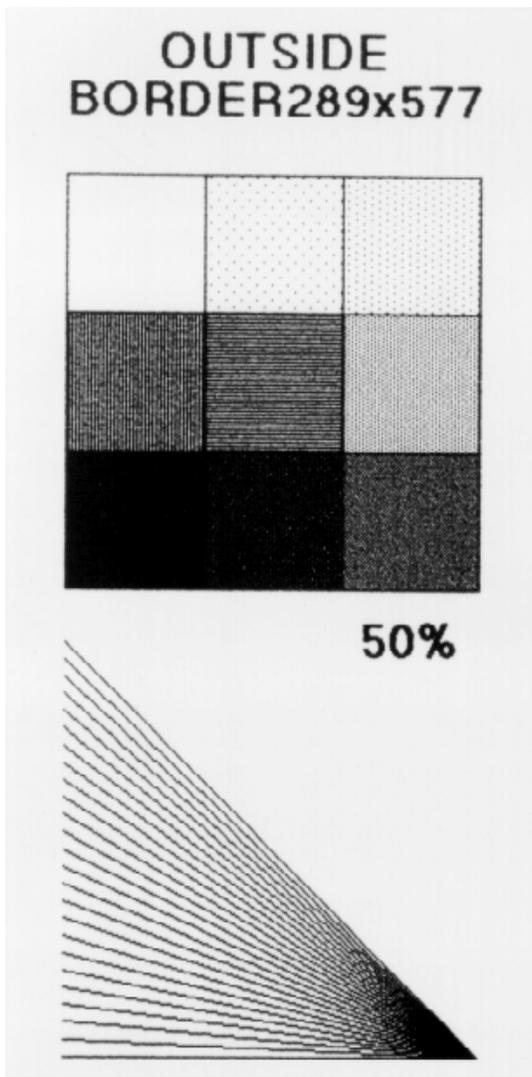
3.5 x enlargement of original print

Figure 9. Test Print of Prototype UV cure ink at 360 d.p.i.

Rapid curing speeds have been obtained such that on-line UV cure is very viable. Trichromatic plus black colour printing has also been demonstrated giving high definition prints with curing being rapid enough to prevent any significant colour-to-colour bleed, even on non-absorbent substrates such as HDPE.

References

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