

Pigmented Jet-Inks for Textile Applications

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Abstract

Textile printing via an ink-jet process is attractive for several reasons:- faster design processes, efficient sampling and the ability for short run production. Development of jet-inks for use in these processes is challenging for the ink formulator due to restrictions in viscosity, particle size and the need for highly reliable jetting. Several authors have described jet-inks for textiles using dye-based approaches. These inks often require post-treatment to achieve satisfactory levels of fastness to washing. As a further consequence, un-fixed dye may have to be removed by a post-washing process. Furthermore, dye selection may have to be altered from substrate to substrate to achieve sufficient levels of fixation. However, much textile is printed conventionally (e.g by screen) with pigmented ink products. These inks generally offer strong resistance properties to water, heat and light as well as providing satisfactory hand and may be applied to a wide range of fabrics.

This paper highlights how a series of jet-inks can perform in a similar manner to traditional textile inks through adaptation of chemistries found in screen textile inks. The jet-inks are water-based, pigmented and latex dispersed. Utilization of a cross-linkable emulsion allows for excellent water-fastness and resistance properties when thermally cured. Colour strength is optimised through usage of specifically designed pigments.

Introduction

Traditionally, textile inks are most often applied by a Screen printing process; the inks are inherently viscous, cover a wide variety of pigment types (including large particle sized metallics), and can offer thick deposits on the material.¹ The resultant application performance of the printed fabrics meets a wide range of stringent criteria such as high temperature washing and dry clean resistance. By contrast, there is considerable challenge in designing jet-inks, with their low viscosity limitations and small particle size, that are capable of meeting similar performance requirements as well as providing satisfactory jetting characteristics. Some authors have reported usage of dye based jet-inks designed for textiles² but these are often substrate dependent and may require further processing steps after printing. This paper gives a description of how water-based pigmented jet-inks for DOD and CIJ print-heads may be designed through careful selection of polymer, pigment and where

appropriate, thickening agent. By undertaking typical textile testing in areas such as crockfastness and wash resistance, it is shown that some of these jet-inks can perform at a similar level to that of traditional screen inks.

Ink Design

Polymer Selection

Water-based emulsion polymers are attractive for usage in jet-ink formulations. Their inherent ability to provide high molecular weight (mwt) materials whilst retaining low viscosity, as well as their environmental benefits are key reasons for this. Furthermore, traditional textile inks typically employed in Screen printing often contain emulsion polymers and these tend to impart good hand and resistant properties to the printed fabrics. An important consideration within emulsion selection is mwt and glass transition temperature (Tg), as both may play a significant role on end properties. A fundamental requirement for jetting performance is appropriate particle size; this ideally is in the range of <1 micron. Usage of mini³ or micro⁴-emulsion polymerisation techniques is a viable route to obtain extremely fine dispersions but in general, standard preparation techniques (with post-filtration if needed) may be satisfactory.

In this study, a series of commercial acrylic and styrene-acrylic emulsion polymers were tested alongside a proprietary optimized acrylic copolymer emulsion, in developmental textile jet-ink formulations. The polymers were selected to cover a range of mwts and Tg's, together with suitable particle size. In the case of the acrylic and styrene-acrylic emulsions, filtration was necessary to remove particles above 1 micron. **Table 1** presents the polymers utilized and appropriate physical data.

Table 1. General Physical Properties of Emulsions

| Polymer | Tg (°C) | Surface Tension | Mwt |
|--------------------------------|---------|-----------------|---------|
| Acrylic + | -8 | 40.0 dyn/cm | 470,000 |
| Styrene – Acrylic ⁺ | 110 | 42.0 dyn/cm | 680,000 |
| Acrylic copolymer ++ | -10 | 38.0 dyn/cm | 300,000 |

+ Available SC Johnson Polymer

++ Available SunChemical

Pigment Choice

Typical pigment dispersions for traditional ink types are often high in viscosity with low surface tension. Adaptation of these to ink jet applications necessitates reduced viscosity, stability considerations, small particle size and the ability to adjust surface tension as required; for typical water-based jet-inks, surface tension should be <35 dyn/cm. Furthermore, the nature of the pigment stabilization groups may play a significant role in ink stability, especially in CIJ inks where a specific degree of conductivity is required for jetting. Usage of a traditional dispersant may cause some difficulty in achieving this. An alternative approach is to attach a stabilizing group directly to the pigment. In some cases, this can result in a more stable ink with lower viscosity. A CMYK set of dispersions was used in the formulations described here. These all exhibit medium-low end viscosities and have adequately high surface tensions to allow for adaptation. In the case of the cyan dispersion, the pigment is specifically modified to achieve lower viscosity than its non-modified counterpart. **Table 2** summarizes some of the physical properties of these dispersions.

Table 2. General Physical Properties of Pigment Dispersions

| Dispersion ⁺⁺ | Viscosity | Surface Tension | Particle Size* D[v, 0.99] |
|--------------------------|-----------|-----------------|------------------------------|
| Cyan | 8.20 cP | 36 dyn/cm | 0.40 μ |
| Magenta | 6.84 P | 35 dyn/cm | 0.30 μ |
| Yellow | 6.52 P | 38 dyn/cm | 0.25 μ |
| Black | 4.82 cP | 57 dyn/cm | 0.20 μ |

⁺⁺ Supplied by SunChemical

* Measured with a Malvern Mastersizer S

Thickener

Given the inherently low viscosity of the emulsion polymers used in these developmental jet-inks, to meet DOD applications especially, incorporation of a thickening agent was made. Four materials were screened:- Propylene glycol, Poly (vinylpyrrolidone) (PVP), Poly (ethylene glycol) (PEG) and a polyurethane thickener (PU).

Crockfastness, hand and washing tests of the resultant inks containing these materials on cotton were made. **Table 3** presents some physical data for the thickeners. Viscosity and pH measurements were made at 20% solids in water.

Table 3. Physical Properties of Thickeners

| | Tg | Mwt | Viscosity | pH |
|------------------|-----------|--------|-----------|-----|
| Propylene Glycol | N/a | 76.10 | 16.1 cP | 7.2 |
| PVP | 180 °C | 66,800 | 25.4 cP | 5.4 |
| PEG | mpt 58 °C | 6000 | 12.3 cP | 7.1 |
| PU | -10 °C | 5500 | 30.2 cP | 7.3 |

Formulations

From the materials described above, a series of CIJ and DOD inks were formulated according to **Table 4**. Thickeners were absent in the lower viscosity CIJ formulations but incorporated in to the DOD series.

Table 4. CIJ and DOD Formulations

| Component | CIJ CMYK | DOD CMYK |
|-----------------|----------------|-------------------|
| Emulsion | 8-14 | 8-14 |
| Water | balance | balance |
| Surfactant | 0.05-1.0 | 0.05-1.0 |
| Humectant | 5-10 | 5-10 |
| Cond Agent | 0.25-0.5 | 0 |
| Thickener | 0 | 0.5-50 |
| Cross-Linker | 0.5-1 | 0.5-1 |
| Pigment | 2-5 | 2-5 |
| Viscosity | 3-5 cPs @ 25 C | 10-14 cPs @ 30 C. |
| Particle Size | <1 micron | <1 micron |
| Surface Tension | 30-35 dyn/cm | 30-35 dyn/cm |

Experimental

The ink formulations were applied to cotton substrate and dried under standard conditions of 150 °C for 3-4 minutes. An Atlas Electric Devices model CM-1 Crockmeter from AATCC was used for ten passes on each print (5 cm x 15 cm) with blank cotton substrate (5 cm x 5 cm) soaked with or without 2mls of water for dry or wet testing, respectively. The samples (10 cm x 15 cm) were also tested in a washing machine for three cycles at 60 °C for 1.5 hours, using Empor Extra M* washing powder. A portion of the prints was removed from the machine after one cycle, for assessment, prior to further washes. A typical grey scale-testing procedure was used for colour fade after testing. The hand of the material was noted subjectively.

* Available Henkel

Results and Discussion

Effect of Polymer Choice

The results from crock and wash testing of various emulsion polymers in cyan DOD formulations against a commercially available screen-ink are presented in **Table 5**.

Table 5. Effect of Emulsion Polymer Type on Crock and Wash Properties assessed by Grey Scale-test**

| Test | Acrylic | Styrene-Acrylic | Acrylic-copolymer | Screen-Ink [†] |
|-----------------|---------|-----------------|-------------------|-------------------------|
| Dry Crock | 1 | 1 | 2 | 3-4 |
| Wet Crock | 1 | 1 | 3 | 2 |
| Washing machine | | | | |
| 1 cycle | 1-2 | 1 | 4 | 4-5 |
| 3 cycles | 1 | 1 | 3 | 3 |

[†] Available SunChemical

^{**} A value of 1 is indicative of poorest performance and 5 is optimum.

Increasing polymer mwt or Tg has no beneficial effect on crockfastness when the acrylic and styrene-acrylic emulsions are used. Furthermore, colour is easily removed in the washing machine test after only one cycle. However, these low levels of crockfastness and washing are considerably improved upon by usage of the acrylic copolymer emulsion combined with cross-linker. The latter material can combine effectively with the acrylic units of the emulsion upon heating. This gives rise to a tough, yet flexible film that is capable of strong pigment binding. The level of crockfastness and wash resistance compares well with a standard cyan Screen textile ink.

Figure 1a-b shows the ease of rub off on cotton fabric under dry (left hand side) and wet (right hand side) conditions of the acrylic and styrene-acrylic based cyan inks. By contrast, images c) and d) show marginal to no rub off under dry and wet conditions. The former contains the acrylic copolymer emulsion combined with cross-linker. This compares favourably with the little amount of ink rub off shown with the Screen Textile ink sample in Figure 1d.

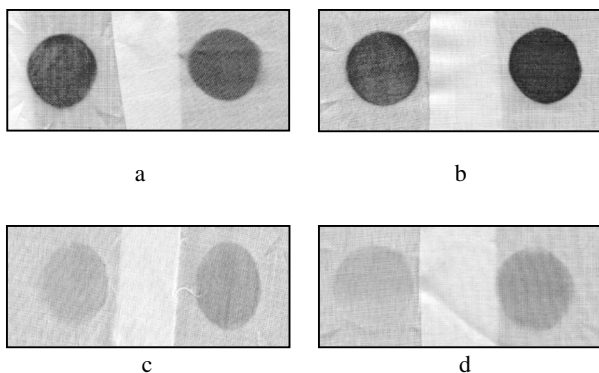


Figure 1. Dry and Wet Crockfastness of a) Acrylic, b) Styrene-acrylic, c) Acrylic copolymer based jet-inks & d) Screen textile ink

The inks based on low Tg (-8 °C) acrylic and acrylic copolymer (-10 °C) provide similar hand to each other (and the screen ink) despite differing somewhat in molecular weight. In contrast, the higher Tg styrene-acrylic (110 °C) imparts a much stiffer feel to the printed fabric despite having a reasonably similar mwt to the acrylic.

Effect of Thickener

For higher viscosity (e.g 10-14cPs at 30 °C) DOD piezo formulations, the thickeners described above were incorporated into the acrylic copolymer emulsion/cross-linker system at various levels. Ideally, a suitable thickener should be fully compatible with the other ink components, have no detrimental effect on ink stability, hand, crock and wash resistance, and be used at a minimum level.

Looking at the results shown in **Table 6**, generally the inks show performance levels in excess of the acrylic and styrene-acrylic analogues (**Table 5**).

Usage of PU thickener at a low level imparts adequate viscosity and gives a strong performance in the dry crock test. However, colour is readily removed under wet conditions. Furthermore, ink stability is not satisfactory over a period of time. Incorporation of PVP results in reasonable dry crock resistance but in a similar manner to PU, performs poorly in washing tests. These two thickeners, due to their nitrogen functionality, may interact with components within the acrylic copolymer emulsion or the pigment dispersion, resulting in instability (in the former case) and easy wash off. Usage of PEG, again at low weight levels, results in an improvement upon wash resistance properties over PU and PVP versions. A further improvement is seen via incorporation of propylene glycol, which due to its non-polymeric nature, is used at higher levels. This thickener provides adequate performance under dry conditions and wash resistance superior to the other thickeners. After three machine washes, colour is retained at the initial level and is equivalent to a typical screen textile ink in performance.

In terms of hand, PU, PEG and Propylene glycol cause no adverse feel to the fabric. In contrast, PVP gives a much stiffer hand. The difference between the PEG and PVP ink performance is most likely attributable to low and high Tg's of 58 °C and 180 °C, respectively.

Table 6. Effect of Thickener Type on Crock and Wash Properties assessed by Grey Scale-test**

| Test | PU | PVP | PEG | Propylene Glycol | Screen Ink [†] |
|-----------------|----|-----|-----|------------------|-------------------------|
| Dry Crock | 4 | 2-3 | 2-3 | 2 | 3-4 |
| Wet Crock | 2 | 1 | 1-2 | 2-3 | 2 |
| Washing machine | | | | | |
| 1 cycle | 1 | 1 | 2 | 4 | 4-5 |
| 3 cycles | 1 | 1 | 2 | 4 | 3 |

[†] Available SunChemical

^{**} A value of 1 is indicative of poorest performance and 5 is optimum.

Pigment Selection & Ink Stability

A key function of the pigments used in this study is their ability to remain stable within the formulation at a variety of temperatures for extended periods. To monitor this, viscosity and particle size measurements of the resultant inks were undertaken at 40 °C and 25 °C over a 3 month period.

As an example, **Table 7** presents the results for a black DOD ink formulation.

Table 7. Stability Data for a Black DOD Ink

| Ink | Particle Size D _[v,0.99] * | | Viscosity 25 °C | |
|----------------|--|--------|-----------------|---------|
| | Initial | Aged | Initial | Aged |
| Black 25 °C | 0.42 μ | 0.49 μ | 11.9 cP | 11.5 cP |
| 40 °C | --- | 0.51 μ | - | 11.7 cP |

* Measured with a Malvern Mastersizer S

The particle size of the ink initially showed 99% of particles were below 0.42 micron. After three months at 25 °C and 40 °C only a slight increase in particle size was noted, with the majority of particles remaining below 0.51 micron.

Viscosity remained virtually constant over a three month period for samples held at 25 °C and 40 °C. Hence this data is indicative of good pigment stability over time.

Conclusion

It is possible to design both CIJ and DOD pigmented, water-based Jet-Inks for Textile applications that can perform in a similar manner to traditional textile Screen inks. To do so, it is necessary to balance the chemistries of the emulsion polymer, pigment and, if applicable, thickening agent. By utilization of an acrylic emulsion copolymer combined with a suitable cross-linker, a distinct improvement was found in hand, wet and dry crockfastness as well as wash resistance, compared with other emulsion polymer types. In combination with an appropriate pigment choice, good stability over 3 months at temperature may be achieved.

References

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Biography

Ally Grant received his PhD in Polymer Synthesis from Cambridge University in 1995. He spent three years as a Polymer Chemist with National Starch before joining Sun Chemical in NJ, USA. There he worked as a Scientist in the Pioneering Technology Group on novel polymers for jet-inks. In 2000 he transferred to the SunJet group in Bath, UK as project leader in new jet-ink technologies. He has five patent applications pending in the field of ink-jet computer to plate.