# Pigmentation of inks for emerging inkjet applications on glass, ceramics and metals

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## Abstract

*Ink jet printing is continuing to move into commercially attractive but technically demanding markets, such as the marking and decoration of glass, ceramics and metals. These markets can require inks with exceptional weather fastness, very high temperature resistance or chemical resistance. The organic pigments and binders commonly used in existing ink jet inks are not sufficiently resistant for such applications. There is therefore a need for jet inks based on stable dispersions of dense inorganic pigments and powdered glass frits. Such inks require a new understanding of jet ink formulation. This paper reviews some of the requirements and looks at how the problems are being resolved to make these emerging applications feasible.*

## Introduction

The printing of glass, ceramics and metals can require inks with a high degree of resistance, to withstand production processing or end-use. Requirements can include high temperature resistance, chemical resistance, very high light fastness, long-term outdoor durability and high opacity. Potential markets include the decoration of architectural glass and metal cladding, marking of industrial components, decoration of ceramic tiles, edge banding of automotive glass etc. The commercial opportunities are significant for digital printing, specifically inkjet printing, in these markets.

Conventional printing inks for these applications are commonly based on inorganic pigments, and may also contain glass frit powders. The inorganic pigment provides highly durable colour and opacity whilst the glass frit, when fused at high temperatures in the production process, provides a binder of exceptional toughness. There is therefore a requirement to formulate stable, jettable inkjet inks with these materials [1],[2].

## Organic v Inorganic Chemistry

The pre-treatment, dispersion and stabilization of organic pigments in inkjet inks have reached a high level of sophistication. This is not the case with inorganic pigments, where there is still a considerable challenge to stabilize very dense, untreated pigments in low viscosity inkjet fluids.

The challenge for inkjet applications can be appreciated by considering the physics of particle settlement in a fluid (Stokes' Law). At equivalent particle size a typical inorganic pigment with a specific gravity (SG) of ~4.5 would settle in a fluid at about 25 times the rate of an organic pigment with an SG of ~1.3.

Titanium dioxide has been used in the ink industry as the white inorganic pigment of choice for many decades. As a result a variety of grades are now available with different surface treatments and highly controlled sub-micron particle size, both of which aid stabilization in an inkjet formulation. With careful formulation white inkjet inks can be produced with little settlement even over prolonged periods of time.

New coloured inorganic pigments and glass frit powders are therefore required with similar sub-micron particle size and surface treatments to facilitate dispersion and stabilisation in inkjet inks. However, existing materials can already be incorporated by high energy dispersion and the use of carefully selected dispersants in the ink formulation. The effectiveness of this approach can be assessed by analyzing the settlement characteristics of the ink.

## Settlement analysis

The settlement rate and the nature (hardness) of settlement in inorganically pigmented inks is crucial to their storage stability and performance in an inkjet printer. These properties can be rapidly evaluated with a Turbiscan device [3]. The following example shows the raw data for a solvent based ink pigmented with a cobalt aluminate blue pigment Colour Index PB28:

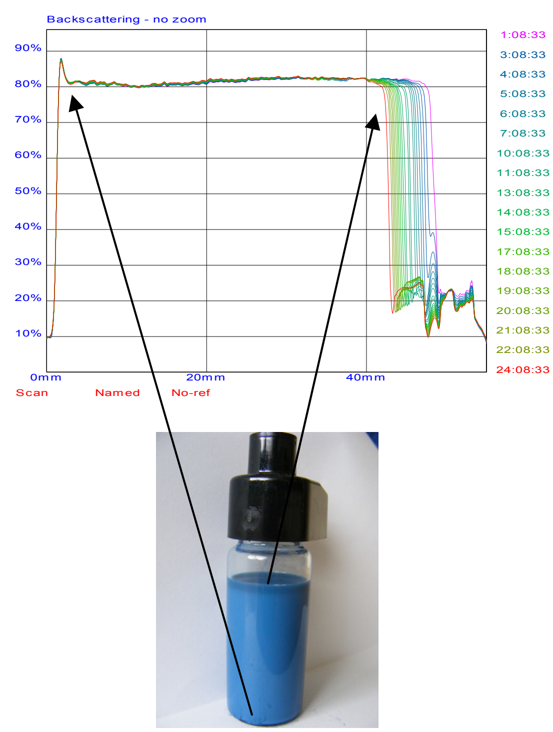


***Figure1**. Time sequence over 24hrs of backscatter curves from the Turbiscan device, along with the visual appearance of the sample after the test*

The average settlement rate during the first 24hrs at the top of the sample can be used as a rapid indicator of the longer-term settlement characteristics of the formulation:

**Table 1: Settlement rate at the top of the sample tube for a range of inorganically pigmented inkjet inks**

| Pigment type (colour index number, chemistry) | Average settlement rate in first 24hrs, at 50degC | Ink chemistry |
|---|---|---|
| PW6 Titanium dioxide | 0.6 μ/min | Commercial UV curing ink |
| PB28 Cobalt aluminate | 10.9 μ/min | Solvent based ink – initial formulation |
| PB28 Cobalt aluminate | 2.4 μ/min | Solvent based ink – optimized formulation |

The amount and physical nature of any sediment can also be analysed using the Turbiscan. In the graph below the data has been referenced to the backscatter curve at time zero. The graph shows a zoom on the curves obtained at the base of the sample tube (0 – 2mm depth). A build-up of sediment is clearly indicated by an increase in backscatter with time. The peak backscatter after 24hrs is actually lower than earlier values indicating that the sediment has reached a critical compaction point. Such compaction could be detrimental to easy redispersibility after prolonged storage:

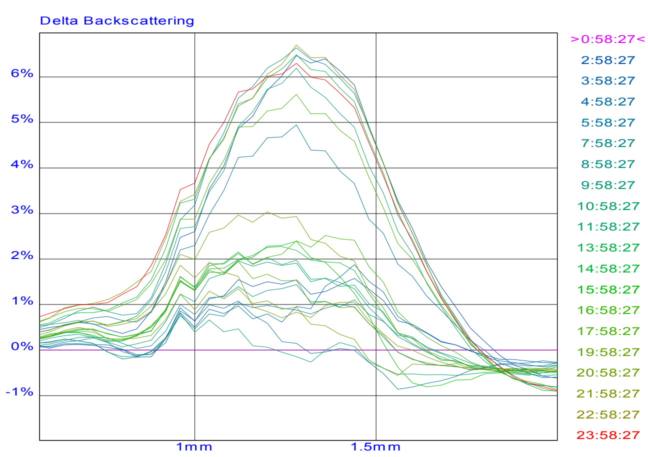


***Figure 2**. Time sequence over 24hrs of referenced backscatter curves from the Turbiscan, taken from the base of the sample*

## Functional properties

Colour and durability are two important functional properties for these emerging markets. The colour specification may vary from a legible code with sufficient colour contrast, to controlled colour values for high quality graphics printing. Durability can be obtained by incorporating glass frit powders into the ink which fuse at high processing temperatures (600 – 1300ºC).

### *Colour*

In common with organic pigments, an improvement in colour might be expected as the particle size is reduced during the pigment dispersion process. However for some inorganic pigments, such as the cadmium based pigments traditionally used in glass decoration, a marked darkening in colour is observed:

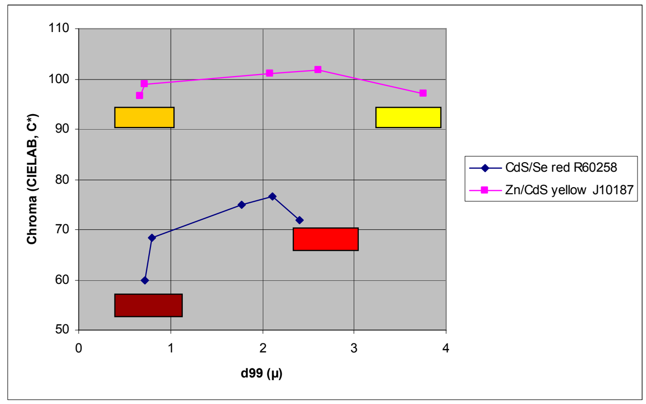


***Figure 3**. Colour development of cadmium pigment dispersions as particle size is reduced, represented by an eventual reduction in colour saturation (C*)*

In other inorganic colour pigment types the selection of the specific pigment chemistry becomes important. For example a range of black spinel pigments have been dispersed in solvent and organic polymer:

**Table 2: Lightness (L*) from inks based on different black pigment types, along with average particle size d50 values**

| Pigment type (CI number, oxide chemistry) | Lightness value (L*) measured on a 12micron thick ink film | d50, in μ. Measured with a Malvern Mastersizer S |
|---|---|---|
| PBl26, Fe/Mn | 4.6 | 0.08 |
| PBl28, Cu/Cr | 17.3 | 0.32 |
| PBl27, Fe/Co/Cr | 34.4 | 0.35 |
| PBl30 Cr/Fe/Ni | 55.3 | 0.42 |

### *Durability - doing away with particles*

A durable print can be achieved without resorting to particulate materials, thus eliminating the difficulties associated with dispersion and stabilisation of inorganic particles. For example, soluble metal salts can be used in the ink, which develop their colour when printed onto an inorganic glaze and fired at high temperatures, such as in the manufacture of ceramic tiles [4].

In a similar way the powdered glass frit which is used as the binder in high temperature coatings on glass and ceramics, can be replaced by an aqueous 'solution' of precursors, typically alkoxides. These develop into a tough, oxide layer once printed and 'cured' at high temperature – the basis of the sol-gel approach.

The use of sol-gels to form inorganic layers is of interest in inkjet applications. They are molecular solutions rather than particulate dispersions, and they can have very low viscosity. Alkoxide mixtures with acceptable storage stability can be formulated, which give films with toughness and opacity when combined with titanium dioxide pigment:

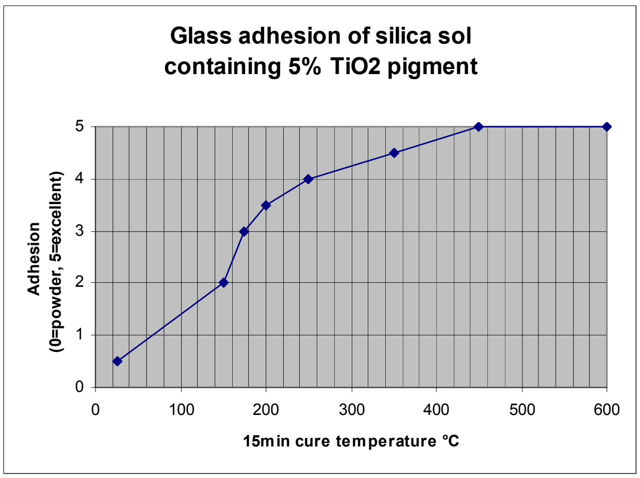


***Figure 4**. Adhesion measured by Crockmeter abrasion test. Glass slide coated with a 12µ layer of a silica-sol containing a titanium dioxide dispersion.*

Such a fluid can, because of its inherent physical properties, be jetted from a continuous inkjet printer to provide a means of marking surfaces which are subsequently subjected to high temperatures as part of the normal production process or end-use:

**Table 3: Physical properties and inkjet printability of a silica sol pigmented with titanium dioxide**

| Viscosity @ 25ºC | Conductivity @ 25 ºC | pH | Particle size distribution | Continuous inkjet printability |
|---|---|---|---|---|
| 3.9cP | 823µS/cm | 2.9 | d50 = 0.32µ<br><br>d100 = 0.36µ | Good printability at 64kHz (70µ print head nozzle) |

The resulting print quality on a sheet of glass is shown in the following Fig 5:

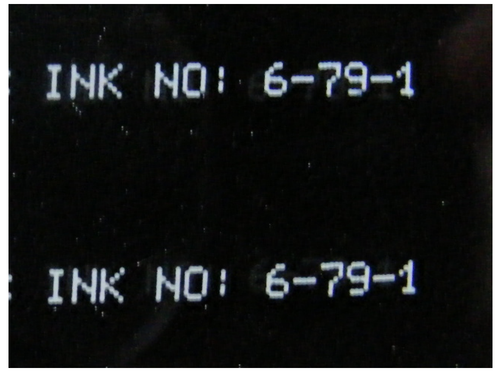


***Figure5**. Photo of a continuous inkjet print of a sol-gel white ink onto glass. For scale the height of the text is ~2mm*

## Conclusion

The printing of glass, ceramics and metals often requires the use of inorganic pigments and even powdered glass frits to provide the necessary levels of durability. The dispersion and stabilization of these materials in inkjet inks is of increasing interest and importance.

It is possible to formulate dispersions of these materials with sufficient settlement and storage stability to make inkjet applications feasible. It is even possible to conceive of chemistries where the need for particulate materials is eliminated.

The successful pigmentation of inks for emerging inkjet applications on glass, ceramics and metals has begun to create significant potential for the use of inkjet printing devices in these markets.

## References


[1] CE-BRITE/EURAM III BE97-4605 "High-Temperature Inks and Computerized Reliable Printing System for Marking and Decoration of Products and Semi-Finished Products"- INCOREDEC.

[2] David Cartlidge, Durable and permanent product identification, authentication and anti-theft marking using inkjet application, Proc. IMI Inkjet as a Manufacturing Process Conference, May 2007.

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[4] Robert A. Harvey et al, Digital Printing Applied to Ceramic Decoration, Proc NIP16 pg 516 – 518 (2000).


## Author Biography

*Hugh Allen is Development Manager in SunJet, a division of Sun Chemical focused on the development and manufacture of ink jet inks. He joined the international printing inks manufacturer Coates in 1985 after graduating in chemistry from Cambridge University. After 13 years in product development and customer service roles for flexographic and gravure inks in both the UK and France, he transferred to SunJet in 1998 and into the new world of digital printing. SunJet is based near Bath, England and Hugh lives near Wells, England's smallest city.*