An investigation into the effects of solvent content on the image quality and stability of ink jet digital prints under varied storage conditions

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Abstract. Increasing numbers of galleries, museums and archives are including ink jet printed materials into their collections, and therefore displays. There is evidence that the instability of these prints is such that images can suffer deterioration in print quality or in extreme cases, a loss of information over an extended period of time. This is shorter than the period typically required for perceptible deterioration to occur in many other paper-based artworks. The image stability of prints is affected by a number of factors some of which have already been studied. However the role played by the ink solvent in the loss of image quality has yet to be explored. This paper will outline research being undertaken to investigate the effects of solvent content which may increase/promote the loss in image quality of the hard copy prints when stored or displayed under a range of temperature and humidity conditions.

1. Introduction

Ink jet digital printing is now well established as a fine art and photographic medium. These images are found in many museums, gallery collections and archives, where longevity of collections is an important issue.

Consumer expectation of image stability for ink jet prints is mistakenly high, due to the standards set by traditional silver halide based colour photography in particular dye destruction processes. The digital print industry is more motivated by production rather than preservation of its products and it is the heritage groups who are most concerned with longevity issues. Importantly, the shortfall in stability of ink jet inks is not generally appreciated by the consumer public who are often unprepared for longer term disappointment.

The image stability of ink jet prints is affected by four primary factors: light, atmospheric pollutants, heat and humidity; in addition, fungal growth and physical damage will also cause losses in image quality.

The roles of light and atmospheric pollutants have been explored and their effects on print stability extensively studied [1, 2]. As a result, procedures for the control of these factors are in an advanced state of preparation [3, 4].

It has been observed that variations in heat and humidity also cause loss of clarity and degradation of image quality in ink jet prints as a result of dye and/or pigment migration in the substrate. The reasons for degradation effects caused by variations in temperature and relative humidity have not been fully established and consequently, conservation procedures have not been standardised; at least three approaches are currently in use [5, 6, 7]. Furthermore, the role of residual solvent in the dye/pigment migration process has not been investigated. This paper will outline the ongoing research being performed by the authors in this area.

2. Ink Jet Inks

Ink jet inks consist of a number of different chemicals designed to improve the printer performance and the quality of the final print. The majority of commercial inkjet printers used for fine art production contain aqueous inks, where water is the primary solvent and accounts for up to 95% (by weight) of the ink. The remainder of the ink will typically consist of the colorant, humectants, surfactant and other additives [8].

Colour in ink jet prints results from the chromophores on either dye or pigment molecules. Optically, dyes scatter little light and therefore provide high saturated colour. They are, however, vulnerable to degradation via UV light and atmospheric pollutants and are relatively sensitive to humidity. Pigment based inks are usually more durable and resistant to environmental factors. However, the relatively large pigment size results in increased surface roughness of the ink layer and causes light to scatter, thereby producing less saturated and duller prints. Pigment particles can also cause clogging of the nozzles in ink jet printers, reducing performance and print quality.

Penetrants are added to the ink to promote penetration of the ink into the paper. These co-solvents also provide shorter drying times for the ink and many also act as humectants, reducing water loss from the ink, so that it does not dry out or clog printhead nozzles. Smooth jetting and penetration of the ink is also aided by the presence of surfactants, which adjust the surface tension of the ink.

Additional components of the ink perform a variety of functions. These include buffers to maintain pH levels, chelating agents to reduce print head corrosion and additives to reduce cockle and curl of the paper fibres.

3. Print Media and Substrate Considerations

The ink-substrate interactions are arguably the most important mechanisms governing print quality. The print characteristics directly resulting from these interactions include optical density, dot size, dot gain, colour, resolution and edge sharpness. These are highly dependent on drop spreading, which is governed by the viscosity and dynamic surface tension of the ink as well as the absorption properties of the substrate. An example of different printed dot morphologies is illustrated in figure 1. [9]



Plain paper

Cast coated



Figure 1. Dot morphologies on different inkjet media

A range of papers can be used with ink jet inks and good printability depends on a number of factors [8, 10]. Plain papers provide the lowest image quality. Due to their high absorbency of water, large areas of print can cause the substrate to cockle and wave. Some spreading of the ink also occurs, resulting in duller and less sharp images. As a result higher performance (and value added) products have appeared such as fine art papers and products with swellable or porous coatings.

Much sharper images are produced by using swellable or porous coated products. Swellable papers can only be used with dye based inks. They work by having a coating which swells to absorb the printed dye. The disadvantage of these papers is that it can take several hours for prints to dry. Microporous papers, on the other hand, have small pores in their coating which rapidly draw water further into the paper, resulting in a print dry to the touch. These papers can be used with both pigments and dyes. SEM micrographs of plain and microporous papers are shown in figures 2 and 3.



Figure 2. SEM image of plain paper



Figure 3. SEM image of coated microporous paper

Finally, fine art papers are made of 100% cotton rag. Image quality is similar to that observed for plain papers. Some manufacturers have coated the papers with a porous ink jet receiver layer to improve the image quality. These papers do not include a resin coated layer.

4. Print Drying and the Role of Solvent

It is believed that it takes a maximum of 8 hours for the water content in an inkjet print to evaporate fully [11]. Although microporous papers appear dry immediately after printing (due to the surface pores), these prints also take time to reach moisture equilibrium with the surrounding atmosphere. Consequently, it has been noted that there is the potential for short term colour drift in the prints in the hours after printing [12]. This indicates the need for conditioning procedures when considering image permanence test methods.

Although the carrier fluid in aqueous inks is principally water, these inks also contain co-solvents. These solvents act as humectants and penetrants, reducing water loss and promoting penetration of ink into the paper. The presence of these co-solvents also impacts the evaporation and drying time of the ink.

While the majority of solvent will evaporate from a print within several days, small quantities of solvent remain in the print for a longer period of time. It is thought that this residual solvent causes the ink dyes and pigments to migrate further over periods of months and years, resulting in loss of image quality and definition. It is also likely that this migration is affected by temperature, humidity and other storage conditions.

5. Background and Previous Work

It is known that both lateral and vertical diffusion of inkjet colourants occurs under variable conditions of temperature and humidity [6, 7, 12-16]. Lateral diffusion results in loss of image clarity due to

uneven, uncontrolled spread of ink across the printed sheet; this is sometimes described as line quality retention. Vertical diffusion of ink into the body of the substrate results in numerous variations to image quality. These include a lowering of image density and gloss as well as loss of colour and variations in colour balance. Additionally, as the different colour process inks exhibit different diffusion properties, undesirable hue shifts can occur due to the uneven migration of the different inks.

Numerous authors have investigated the effects of humidity and temperature on the final print [17, 18, 19]. Dye based prints have shown increased susceptibility to changes in humidity, particularly when printed on a swellable medium [7, 15]. In contrast, pigment based inks appear to be relatively stable although studies have shown that they can demonstrate migration under conditions of high humidity [20, 21]. Substrate properties also affect the permanence of the final print. Research has shown that the fluorescence of whitening agents in the paper is affected by temperature but not significantly by humidity [22].

These factors all have adverse effects on the ability to maintain a stable, consistent hard copy and present problems for museums and galleries with the storage and display of works of art produced using ink jet inks. In addition, digital ink formulations involve the inclusion of high boiling point solvents such as glycols which improve ink mobility within the print head but further complicate the diffusion processes in the printed hard copy.

Research to date has only studied the consequences of these changes and has not attempted to explore what is happening within the printed system. It is envisaged that effect of solvents and dye/pigment properties together with the structure of the substrates and changes in temperature and humidity will all play a part in affecting the degree of dye/pigment migration.

Previous studies by Steiger and Brugger [23] found that residual solvents in dyes can decrease their fastness behaviour. This is thought to be because of a reduction in dye aggregation resulting from continued diffusion of the solvent through the substrate. Research by Wilhelm [11] has investigated the lightfastness of ink jet prints under differing drying conditions. It was shown that the light fading of prints can display very different behaviour depending on the drying conditions involved. In the case of the magenta dye, contact drying of prints results in better light fastness than air drying. This is possibly a result of the contact drying removing the residual solvent content in the print, suggesting that these reduce dye aggregation and therefore lightfastness.

This research will examine the effects of temperature and humidity on the rates of diffusion that occur for different process colour inks on a range of substrate types. The role of the solvent will be closely examined because this will play a major part in dye diffusion. It is hypothesised that the solvent will continue to diffuse through the paper after drying, resulting in the migration of ink dyes and pigments further into the substrate over time. It is also hypothesised that lateral and vertical migration of these pigments and dyes could, with time, result in a decrease in line quality and sharpness as well as colour and balance, affecting the quality of the image as a whole. The controlled removal of solvent will be explored as a means to stabilise prints under all conditions of exposure to relative humidity and heat, rather than simply storing them under standard conditions where deterioration will still occur.

6. Experimental Method

In order to conduct tests for differing levels of humidity fastness, a range of inks and substrates will be used to evaluate the effect of solvent content. These will include both dyes and pigment based inks as well as swellable, microporous and fibrous papers. Ink jet prints will be obtained from commercial printers who are able to reliably print and store under controlled conditions of temperature and relative humidity. These prints will be allowed to condition at constant temperature and relative humidity before being subjected to test methods.

The test images will be selected to objectively measure colour changes and loss in line quality. The printed image will include two picture elements to enable comparative visual assessment coupled with a target. The target will include a half-tone chequer-board pattern of colours similar to that used by Kaimoto and Shibahara [13] to record the edge definition and image area. These measurements will be

made using optical microscopy coupled with image analysis. Changes in the density, gloss and hue of each colour patch will be recorded in order to monitor colorant migration. Solid colour targets will also be included to enable the extent of vertical ink diffusion to be recorded using scanning electron microscopy. All combinations of the four process inks will be studied to assess the effects of interactions between them.

The relative solvent content of the samples will be initially measured using a variety of techniques to establish the most effective. The techniques include Fourier-transform infra red spectroscopy (FTIR), thermal analysis techniques of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and gas chromatography.

Following analysis, half the samples will be sealed in impermeable enclosures to ensure no loss of solvent to the storage atmosphere. One third of the sealed and unsealed samples will be stored under known temperature and relative humidity conditions as recommended in BS5454. These samples will constitute the control groups. A second third will be further subdivided and each sample stored at different temperatures and relative humidity conditions ranging from 20°C to 80°C and 20% to 80% RH; this will also enable an assessment of the impermeability of the enclosures. The final third of samples will be subjected to a range of treatments to remove or reduce the ink solvent content before storage under the same conditions. Methods to remove residual ink solvent from the prints will include the use of a degasser and absorbent contact drying of prints. The reduction in solvent content will be monitored using FTIR, thermal analysis and headspace analysis gas chromatography.

Stored samples will be measured at regular intervals up to a total storage time of two years. Changes over this period are known to occur from light fading studies [7] where changes have been detected over 24 months. Measurement techniques will be densitometry and glossmeter for changes in image density and gloss, and colorimetry for hue shift. Changes from the initial measurements will be plotted on logarithmic scales and analysed using the well established Arrhenius method [24]. The picture elements will permit subjective assessment of perceptible changes in image quality by a panel of observers.

Correlations will be sought between residual solvent content and changes in colorant migration, density and hue shift. If such a link is established, procedures for long term preservation of prints will follow.

7. Conclusion

Research findings from the project will provide information about the role of residual solvent in the migration of ink in papers over long periods of time. The findings will benefit two audiences, those producing ink jet prints and those responsible for the safe keeping of such prints. The first group comprising artists, commercial printers and domestic users who will be informed of the published protocols and guidelines to ensure the minimum deterioration of their ink jet prints. The second group, comprising conservators and curators will have recommendations and guidance on how best to store and display artefacts containing ink jet prints.

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