Colour changes in prints during long-term dark storage of prints

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Abstract. The most significant impact on colour fading in prints is exposure to light and air. However what happens to coloured prints during long-term storage in boxes, drawers and on shelves? Measurements of samples, printed in July 2005, stored in a range of light and darkened storage conditions have shown some interesting initial results. As more emphasis is placed on the effects of light, the dark stability of inkjet prints is relatively overlooked when considering how to preserve or store coloured prints. This study and presentation builds on previous research [1] and has concentrated on the changes to colour during storage. With reference to ASTM F2035 - 00(2006) Standard Practice for Measuring the Dark Stability of Ink Jet Prints, the Standards outline points out that whilst natural aging is the most reliable method of assessing image stability, materials and inks any data that is produced quickly becomes redundant; therefore accelerated aging is more preferred. However, the fine art materials in this study are still very much in circulation. The leading fine art papers, and pigmented ink-sets used in these trials are still being used by artists. We can therefore demonstrate the characteristics of colour changes and the impact of ink on paper that utilises natural aging methods.

1. Introduction
With the emergence of digital imaging technologies in the 1980s, there followed a desire to print high quality colour images for artists. When Graham Nash and Mac Holbert, of Nash Editions USA, began printing using a Scitex Iris (3047) printer they realised that whilst the Iris technology produced beautiful, rich and dense colour, the dye-based inks were fugitive. They found that the early inks, if left in daylight for a few hours would fade. [2]

In Bristol in the late 1990s work with the Encad Novajet also confirmed these fears. Tests revealed that dye based inks were of such a fugitive composition that when printed on standard coated cheap paper stock, they could fade perceptibly if left in the open air and even in a dark room overnight. The problem of colours changing in the dark suggested other important contributory factors such as ozone or gas fading, which might be generated by air circulated from fans, or an open window. As more digital work began to be printed onto coated papers, the question of the compatibility between papers and inks became more urgent. This has been an ongoing problem, echoed by Henry Wilhelm’s paper How long will it last? An overview of the light-fading stability of inkjet prints and traditional color photographs. [3]

The most significant impact on colour fading in prints is exposure to light and air. However what happens to coloured prints during long-term storage in boxes, drawers and on shelves? Artists working
at the Centre for Fine Print Research are engaged in a range of digital printing and paper construction. This has included large-scale printing, and might be combined with other materials, such as stitching, screen inks, other printmaking processes, embossing and the surface of the paper might be dampened. These artworks might be stored in portfolios, in drawers, dry-mounted and unframed. The majority of prints are stored in boxes, but in some cases even in the dark as paper and images began to discolour, the stability of the prints began to be questioned.

2. Background and previous study 2005-2006 [1]
The original study (2005-2006) measured the changes to the whiteness of paper. Prints were stored in different conditions, which were monitored and measured eight times over ten months. Since 2005, the storage of these prints has continued in the same conditions and a new set of measurement data has been collected (2009-2010). In order to gain a thorough understanding of the long-term effect of the storage of prints: in drawers, boxes, open on a shelf or in plastic the emphasis here has moved from the measuring the whiteness of the paper to comparing the colour patches at the top and bottom of the piles. The papers containing OBAs showed an initial rapid drop off in brightness, with relatively little subsequent change occurring. At the end of the first study period (2006), colours and papers were compared and in some cases the average data gave negative results, suggesting that instead of fading, colours and papers were darkening. Hypotheses and questions arose when analysing the data, the assumption being at the time, there were anomalies in the paper surface, human error or problems with the equipment or calibration.

Other hypotheses concerning darkening of the paper samples [4] suggest that it was the paper that could be the problem. Papanagiotou described Japanese paper as indicating a darkening or yellowing, suggesting that the fibre content can contribute to colour difference. In previous accelerated lightfast pilot tests (1999) the surface of coated papers became yellowed, although this has not occurred during any real–time tests. Different manufacturing processes, such as the texture, sizing and construction of the paper may also contribute to colour changes. Yellowning of paper during storage is also considered by Mitsubishi paper mills [5]

Wilhelm research concurs also that ink is not necessarily the main problem, but the paper can affect the stability of an image. Their findings also suggest that humidity can cause changes to prints, such as colour darkening and an increased chroma instead of fading. Humidity in the UK is problematic and with an increase in erratic weather conditions and damper summers then more emphasis should be placed on how prints are stored [6].

Saunders gave examples [7] of some characteristics of fading and changing in fine art pigments as a result of the impact of atmospheric conditions. Organic dye-stuffs and lake pigments are highly fugitive. For example, Rose madder is known to fade within a few months if exposed to strong light, although darker tones are more permanent. In a fresco, lime destroys madder completely. There are less common occurrences of fading in inorganic pigments, but are more likely to darken, which is due to the existence of salts in a humid environment. For example, red lead can darken when exposed to humidity and light. It can also lighten in fresco paintings due to an interaction with moisture and atmospheric pollutants. Also a result of the existence of, and the capillary action as salts are drawn through walls, azurite - a deep blue copper mineral - can turn green.

The objective therefore was to continue with the testing of existing pigment and dye samples. We decided to continue with the samples with dye based inks as well as pigment, as this is still being used for many desk-jet photo printers. This is due to the brightness of the colours and being able to achieve the appearance of a full colour image using just four process colours. However for this paper we shall report on just the pigment samples.

2.1. Brief description of differences between pigments and dyes
Pigments are finely ground coloured particles that are suspended in a carrier liquid. In contrast to dyes, which colour by staining materials, pigment particles sit on top of a material surface. However, in inkjet printing the objective is to maintain the dye and pigment colourant on the paper surface by using
a receptor layer [8]. It is generally considered that permanent inks are usually made with pigments and non-permanent inks are made with dyes.\(^1\) Furthermore, dyes are composed of organic materials that are more susceptible to fading than pigments, which are made from inorganic materials. Synthetic organic pigments tend to be more lightfast than their natural organic counterparts, they are highly saturated and can be used as an extender to the replace larger proportions of inorganic pigments; thus reducing manufacturing costs. Based on past experience of inkjet dyes of the past, early inkjet inks were dye based inks and faded in a relatively short space of time. However, as greater demands and with technological developments in high performance dyes and pigments, these definitions are beginning to be blurred. In very broad terms, many materials exist with a range of solubility and permanence; pigments at the low end and dyes at the higher end. Many definitions are not precise because of highly sophisticated manufacturing methods, for example pigments that have been ground to such ultrafine particulates could be considered as a stain. Furthermore, materials must be able to be resistant to light, moisture, air, alkalis, acids and also resistant to heat and pressure of an inkjet printer head system. These highly specialised materials are required for high performance applications that are very different to the traditional watercolours and paints as used by artists.

Some typical examples of organic and inorganic pigments are listed here: [9] Organic: a) vegetable source (indigo, madder); b) animal source (sepia, cochineal); c) synthetic organic (phthalocyanine blue, alizarin crimson). Inorganic: a) Native earth (raw umber, raw sienna); b) Calcined native earth (burnt umber, burnt sienna); c) Synthetic inorganic colour (titanium dioxide, cerulean blue).

There is a huge range of pigments from which to choose and for the inkjet chemist the important factor is to choose a colorant that when intermixed, the purity of colour is maintained. A cyan, magenta, yellow and black inkset may comprise a cyan ink that contains the chemical properties of a phthalocyanine pigment, the magenta ink composition may contain the quinacridone pigment, and the black ink is a carbon black, which is the most most resistant to fading and which can withstand visible and ultraviolet light, moisture, air\(^2\).

2.2. Improvements in inkjet inks
Since 2000, inkjet inks have been developed for a higher degree of permanence. The cheaper and less permanent inks fulfil a necessary role for major sectors of the industrial and office market, and the high end fine art market inks have significantly shifted from dye based to pigment based inks. Pigment inks have brought the longevity of printed output in line with standards established in the high-end museum quality print market.

Although dye based inks present a more saturated colour gamut, it has been necessary from our bias at the CFPR towards high quality fine art printing to utilise the highest quality pigment based inks. Although pigment inks are less intense than dyes, they are more resistant to UV and gas fading. The pigment molecules are more complex and break down at a slower rate than the simpler, small molecule dyes. Whilst early pigment inks lacked intensity, advances have been made to improve the quality of these inks. This shift has developed in response to user demand for archiving and colour longevity, especially for the production of large print works, including exhibition, display and the fine art and poster market, where it is essential for colours not to fade.

For the medium and wide-format market, the initial four CMYK ink sets have recently been expanded to eight and twelve colour sets. For example Canon’s LUCIA Pigment Ink Technology

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\(^1\) Some inkjet manufactures describe their inks-sets as pigmented although they add a proportion of dye to enhance the saturation of the colour.

\(^2\) For more information on the main families of pigments go to: http://www.specialchem4coatings.com/tc/color-handbook/index.aspx?id=families also for longevity of artists pigments go to Bruce MacEvoy’s Handprint website (2006) http://handprint.com/HP/WCL/waterb.html#PB27
contains twelve-colour inks (a mixture of pigment and dye colours) using CMYK and red, blue, green, grey, photo grey, photo cyan, photo magenta, and matte black. Hewlett Packard have introduced their Vivera range of colours to their new Design Jet Z series, which includes CMY plus light grey, grey, matte black and photo black, orange/red, blue, green, light magenta and gloss. By adding colours to the existing colour set to address gaps in the colour gamut, the inclusion of green has resulted in the light cyan being redundant.

Epson’s UltraChrome colour system has included two different black ink modes - photo black and matte black; Canon differentiates between matte black, regular black, grey and photo grey. According to Canon, the combination of both grey and photo grey enables smoother transitions from light to dark. Hewlett Packard have included four grey/blacks, with the addition of a gloss. As part of their media profiling management system this can be switched on or off to enhance density and is an automatic component of gloss papers.

Epson UltraChrome ink incorporates a High-gloss Micro-crystal Encapsulation, in which, according to Epson literature, each pigment is coated in a resin to reduce the grouping of pigment particles. This is similar to Hewlett Packard’s Vivera Electrosteric Encapsulation Technology or EET; negative electrostatic charges are introduced within the resin layer, which coat the pigment particles and prevent them clumping together.

2.3. Developments in colour change testing
Over the last ten years, the quality of inks and papers has vastly improved, as has the print technology. Printer manufacturers, have guaranteed print longevity of more than 100 years. However, a test by Wilhelm established that the compatibility of paper and ink had a significant impact on the life expectancy of the image. For example, if the same manufacturer ink, paper and printer were used there was hardly any visible difference over 25 years. However, using a different paper with different inks and printer resulted initially in a reduced gamut image and image degeneration in less than 3 months. For artists using fine art papers on a range of machines, this could have important implications for the longevity of their prints.

An significant introduction to the standards for inkjet permanence is the testing for the dark stability of prints. In the introduction to the Standard, ASTM F2035 - 00(2006) Standard Practice for Measuring the Dark Stability of Ink Jet Prints, suggests that natural aging is the most reliable method determining time and understanding the changes in stability. However it points out that materials and technology are quickly updated and replaced and therefore data can become redundant.

It seems however in the last few years the inkjet market has begun to mature and fewer dramatic changes have occurred. New fine art papers have been introduced and extra colours added to the inkset, however for the artists’ print market the majority of materials are still in circulation and therefore it is possible to undertake natural aging experiments. Our measurements undertaken in 2005 still have relevance.

In the standard ASTM F2035 - 00(2006) the suggestion is that Arrhenius testing is a good long-term predictor for long-term dark storage. This procedure involves increasing the temperature at a constant relative humidity. In order to test for long-term dark storage stability the Arrhenius testing method is undertaken by Wilhelm research, and is described in more detail here [6].

3. Methodology
Following the question “What happens to the prints at the bottom of a pile?” A method was devised to ascertain changes to the printed colour when displayed and stored in different conditions. Different types of papers (Somerset Enhanced, Somerset Satin (uncoated) Hahnemühle William Turner, Hewlett Packard Gloss) were subjected to a range of conditions (open on a shelf under low light conditions, wrapped in plastic, stored in an archival box). Piles of prints were arranged to simulate how a print

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3 www.astm.org/Standards/F2035.htm
might fare at the top of a pile compared to the bottom of a pile. These piles were placed in archival print boxes, open on a darkened shelf and wrapped in plastic print bags. Using a CMYKLCm colour set, an edition of 10 prints per test pile were printed onto the four test papers. Each test sheet measures 100 x 150 mm and contains 91 colour patches: CMYKRGB from 5% -100% colour and 100% colour with 20% increments of black. A clear space is also included for measuring the spectral reflectance and changes to the whiteness of the paper.

Each paper was coded according to the ink, paper and placement. For example, a sample labelled: ab301 describes a pigment inkset that is printed onto Hahnemühle William Turner paper, which is placed at the bottom of the pile.

**Table 1. Codes used for position of the print and paper type**

| Position of pile | Paper                                |
|------------------|--------------------------------------|
| 001 shelf top of pile | ad Somerset Enhanced pigment printer |
| 002 shelf bottom of pile | bd Somerset Enhanced dye printer |
| 101 plastic top of pile | aa Somerset Satin pigment printer |
| 102 plastic bottom of pile | ba Somerset Satin dye printer |
| 201 frame | ab Hahnemühle W Turner pigment printer |
| 302 box bottom of pile | bb Hahnemühle W Turner dye printer |
| 301 box top of pile | ac Hewlett Packard Gloss pigment printer |
| 401 open air | bc Hewlett Packard gloss dye printer |

**Figure 1. Test chart designed for CMYK printer.**

3.1 Measuring (2005)
The original study began in July 2005 and using the Gretag Macbeth Profile Maker Pro measuring tool software, a custom target of 7 x 13 patches, including a space to measure the paper, was generated. From this the measuring data was saved as spectral and CIEL*a*b* formats. The first set of measurements was used as the reference data, and ten sets of measurements were undertaken over an
eight-month period. Measurements were made to the paper and colour patches of the printed sheet on the top of the pile and the print at the bottom of the pile. Initial measurements for this study were taken in October 2009 and have been updated in February 2010. Over the course of measuring, initial negative values demonstrated early indications that colour and paper has darkened over time. Early suggestions for these negative results included human or measuring error, but as a result of re-measuring and rechecking data, and after 3 further years of storage the reflectances show a clear indication of darkening.

In the previous study and paper, the effect of optical brighteners was explored and considered against Tappi and CIE whiteness. The whiteness differences between the papers was measured at the beginning of the test and at the end of the test period. At the same time, a series of measurements were undertaken to 100% colour patches along the top of the printed test charts.

3.2. Measuring (2009)
Although measurements were taken for the pigment and dye samples, for this paper, we will concentrate and report on pigment materials and printers. Therefore two fine-art inkjet receptive, one uncoated fine art printmaking and one photo gloss pigment receptive paper was measured. All of the prints are stored in the same room, which has both natural (non direct) light and fluorescent strip lighting. The room, and consequently the prints, have been subject to variable lighting and heating condition for 43 months. The temperature has therefore ranged from a hot humid summer day to a cold winder day with no heating. The Gretag Macbeth Spectrolino with UV filter standard illuminant of D50 and 2º colorimetric observer has continued to be used for these measurements. Differences are calculated between the reference data from July 2005 and the most recent set of data.

4. Results
As initial measurements and comparisons in 2005 showed a peak in the violet region of the photo-gloss paper sample, a UV filter was used for measuring all the paper samples. From the new data, we have been able to compare any changes occurring to colour patches at the top and bottom of the piles. The following figures show the differences between the original (2005) measured paper sample (an unbroken line), a print at the top of the pile (identifiable by a line intersected by squares) and a print at the bottom of a pile (identifiable by a line intersected by circles). The results demonstrate that paper samples kept out of the light have not faded but have darkened. In some cases this has occurred very slightly as demonstrated in samples kept in plastic. In other cases where samples have been kept open on the shelf samples have darkened considerably more. Samples open on top of the shelf had darkened more than the samples at the bottom of the pile.

5. Conclusion
The paper, through colour measurements and spectral graphs has compared the original data (2005-2006) and a new set of measurement data (2009-2010). All of the prints are stored in the same room, which has both natural (non direct) light and fluorescent strip lighting. The room, and consequently the prints, have been subject to variable lighting and heating condition for 43 months. The temperature has ranged from hot humid summer days to cold winder days with no heating. Whilst this does not present an ideal or quantifiable condition for the maintenance of prints, it does represent typical storage conditions in art and photographic studios, art departments, universities, libraries and homes. For archive conditions such as galleries, museums, archives and repositories it is unlikely that effects of ozone and humidity will impact collections.

The samples were kept in the same conditions as the previous tests: in drawers, boxes, open on a shelf and in plastic. As exampled, when comparing papers at the bottom and top of open piles, the colours and fine art papers (Somerset Enhanced, Hahnemühle William Turner, Somerset Satin) on the top of the pile had darkened. This might be due to the combination of ozone, humidity and dirt on the paper through the collection of dust. It is interesting to note that as shown in figure 2, which are details from
figures 4 and 13, the Somerset Enhanced sample on the top of the pile darkened more than the corresponding sample on the bottom of the pile, whereas for the gloss sample the situation is reversed. This might be due to the lightening of the gloss paper sample. As shown in figure 3, which are details from figures 7 to 9, a comparison shows larger differences between Somerset Satin paper samples stored on an open shelf, than those stored in plastic or the box. The Satin (which is not coated) paper may have become dirty over time or the fibres in the paper evenly changed through aging. This also has a correlation to the colour changes for all the printed colours on the Satin samples, which appear to have become darker. As described by Saunders, there is a similar occurrence between contemporary printed samples and traditional dyes and pigments as used in paintings and frescoes; these react to salts and pollution in the air. Even for samples that are kept in boxes (albeit there are only minute changes), there is still enough humidity to cause an effect on both the paper and the coloured samples.

Figure 2. Somerset Enhanced papers on open shelf compared to gloss samples on shelf.

Figure 3. Comparison of Somerset Satin paper samples (top) open shelf, (middle) plastic, (bottom) box.
Figure 4. Colour measurements of gloss paper, open on shelf, top and bottom of the pile.

Figure 5. Colour measurements of gloss paper, wrapped in plastic on a shelf, top and bottom of the pile.
Figure 6. Colour measurements of gloss paper, stored in a box, top and bottom of the pile.

Figure 7. Colour measurements of Somerset Satin paper, open on shelf, top and bottom of the pile.
Figure 8. Colour measurements of Somerset Satin paper, wrapped in plastic on a shelf, top and bottom of the pile.

Figure 9. Colour measurements of Somerset Satin paper, stored in a box, top and bottom of the pile.
Figure 10. Colour measurements of Hahnemühle William Turner paper, open on shelf, top and bottom of the pile.

Figure 11. Colour measurements of Hahnemühle William Turner paper, wrapped in plastic on a shelf, top and bottom of the pile.
Figure 12. Colour measurements of Hahnemühle William Turner paper, stored in a box, top and bottom of the pile.

Figure 13. Colour measurements of Somerset Enhanced paper, open on shelf, top and bottom of the pile.
Figure 14. Colour measurements of Somerset Enhanced paper, wrapped in plastic on a shelf, top and bottom of the pile.

Figure 15. Colour measurements of Somerset Enhanced paper, stored in a box, top and bottom of the pile.
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