

SCIENTIFIC PAPER

HUMIDITY SENSITIVITY OF INKJET PRINTS

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One of the potential aspects of the degradation of digitally printed images is their sensitivity to elevated humidity. Inkjet prints in particular have been shown to exhibit humid bleed. Studies into the humidity stability of inkjet prints have led to the development of an ISO standard to test humidity fastness, published as ISO 18946:2011. This paper details the use of this methodology to examine the humidity sensitivity of a number of contemporary ink-media combinations in use ca. 2000-2010. Two environmental exposure conditions were used: 25 °C, 85% RH and 40 °C, 80% RH. We find that the extent of humid bleed varies widely depending on the ink-media combinations and the environmental exposure conditions. In particular, swellable papers printed with dye-based inks are found to exhibit pronounced humid bleed, while plain and archival papers are found to be less susceptible to conditions of elevated humidity. However colorimetric measurements indicate that both pigment and dye-based inks show some colour change when printed on the latter papers. This work provides valuable information regarding the comparative stability of inkjet prints, many of which make their way into heritage collections and archives.

1 Introduction

With increasing numbers of digitally printed materials making their way into archives and heritage collections, either as unique items with aesthetic value, or as carriers of information, there is concern about how these materials will deteriorate over time.^{1,2} Digital prints may be susceptible to various environmental factors, and their sensitivity to elevated humidity is one of the mechanisms by which these prints may degrade. The influence of humidity on image bleed, and the sensitivity of inkjet prints in particular, has been well documented.³⁻⁶ These studies have used various methods to characterise the humidity sensitivity of inkjet prints and this substantial experimental evidence has aided the development of an ISO standard test method, published as ISO 18946:2011.⁷ An evaluation of the use of this standard to test humidity stability has previously been published.⁸

In a print, colorant migration can occur in both the lateral and vertical directions. Dye-based inks are thought to be more susceptible to humid bleed, but there is evidence that change also occurs with pigment-based inks. The properties of the substrate can also contribute to humid bleed,

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with the presence and type of coating affecting the movement of the colorant. In addition, the substrate may demonstrate yellowing,³ further contributing to changes in image quality.

A number of contemporary ink and media combinations in use ca. 2000-2010 will be examined in this paper. Both dye and pigment-based inkjet inks will be used to illustrate the work: the latter are more lightfast, and find wide application in documents intended to have archival value. Dye-based inksets in general offer a wider colour gamut and are often cheaper than pigment-based inksets: they are used for printing photographs and for many types of printed output intended not to have a long life. Such items however do enter archives. The paper will compare and contrast the results from different humidity test conditions described in ISO 18946:2011; variations in the humidity sensitivity of different areas of the test target will also be examined. Changes in image quality resulting from humidity exposure will be presented as colorimetric data and as photomicrographs.

2 Experimental

ISO 18946:2011 details a test method to examine the humidity fastness of inkjet prints. The test chart described in this standard is similar to that used by Kaimoto and Shibahara⁵ and consists of 84 individual swatches incorporating both solid and checkerboard areas to evaluate lateral and vertical bleed (Fig. 1). It also contains areas of full and light density as well as flesh tones and alphanumeric characters. In addition, unprinted areas allow for the evaluation of paper yellowing. ISO 18946:2011 stipulates that three humidity test procedures may be used; this work uses the fixed humidity method. In order to quantify the extent of bleed, and therefore sensitivity to humidity, the $L^*a^*b^*$ values for each swatch are measured before and after environmental exposure to a specified humidity condition. The ΔE^*_{ab} values for each swatch are then calculated in CIE 1976 $L^*a^*b^*$ colour space before being averaged over all 84 colour swatches to produce a final value, Ave ΔE , for each sample. It is worth noting that the colour changes measured on the checkerboard areas after humidity exposure correlate with loss of line quality and provide an indirect measurement of lateral colour bleed.⁷ There may also be vertical movement of the colorant through the substrate.

In this work, prints were produced on four different substrate types, as detailed in Tab. 1. These types of substrates were thought to be of particular interest to the conservation and heritage communities. In particular, the archival paper is of interest because it is specifically marketed as a substrate that will be stable for a long period of time. The other substrates are commonly used in both business and domestic inkjet

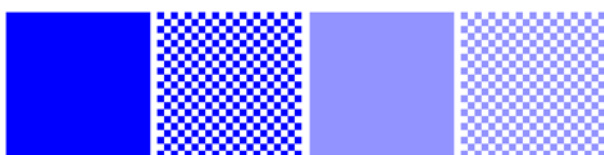


Figure 1: Example of sections of the test chart, showing solid and checkerboard swatches at full and light density. The dimensions of each swatch are 6 mm x 6 mm.

Type	Description	Date of availability
Plain paper	95 g/m ² uncoated paper without optical brighteners	ca. 2008
Archival paper	85 g/m ² , off-white long life archive text paper Hot extract pH 9.4, minimum of 2% CaCO ₃ , fully bleached chemical woodpulp paper	ca. 2010
Swellable paper (A)	Coated 100 μ m polyester film Gelatine coating	ca. 2000
Swellable paper (B)	240 g/m ² classic glossy resin coated inkjet paper Gelatin coating	2010
Microporous paper (C)	260 g/m ² premium glossy resin coated inkjet paper Microporous silica coating	ca. 2006
Microporous paper (D)	280 g/m ² smooth gloss inkjet paper Microporous mineral coating	2010

Table 1: Substrate details.

printing and are therefore likely to be found in collections. Plain and archival papers have uncoated surfaces and can be used with both dye-based and pigment-based inks and tests were undertaken with both. Swellable media are designed for use with dye-based inks only (they cannot be used with pigment-based inks) and consist of a swellable layer on the surface of the paper which encapsulates the colorant as it dries. Tests were only undertaken using dye-based inks. These papers have a long drying time and are sensitive to high humidity. The surface of a microporous paper is covered with tiny pores which absorb the colorant. These prints are dry to the touch immediately after printing and are generally less sensitive to high humidity. Microporous papers may be used with both pigment or dye-based inks and tests were undertaken using both.

The substrates were printed using both dye and pigment-based inks from the original equipment manufacturers. Widely-used printers for documents were included to cover both fine art prints and archival material. The details of the printers and inksets used in this work are shown in Tab. 2. The order of the inksets listed in Tab. 2 bears no relation to the numbers used in the later Figures.

Printer	Inkset	Date of availability
Dye-based		
Canon iP4700	Dye-based CMY Pigment-based K	2009
HP PSC 2210	Dye-based CMY Pigment-based K	2002
HP PSC 2210	Dye-based CMYK Lc, Lm	2002
HP Officejet Pro K5400	Dye-based CMY Pigment-based K	2007
Pigment-based		
HP Officejet Pro 8000	Pigment-based CMYK	2009
Epson Stylus Photo R800	Pigment-based CMY Pk, Mk, R, B	2004
Epson Stylus D88	Pigment-based CMYK	ca. 2005

Table 2: Printer and inkset details.

Samples were printed in an environment of 23 °C and 50%RH on substrates that had been allowed to acclimatise to these conditions. After printing, the samples were air-dried for 24 h, before being placed in a Weiss Gallenkamp environmental chamber and exposed to one of two separate environmental conditions defined in ISO 18946:2011:

- A high humidity condition: 25 °C, 85% RH
- A high humidity, high temperature condition: 40 °C, 80% RH

During the humidity exposure, the samples were suspended from shelves using metal clips. Weights were also attached to some samples to reduce the substrate curling during exposure.

The samples were removed from the chambers after an exposure period of 1, 2 or 4 weeks and allowed to return to environmental conditions of typically 23 °C, 50% RH for a period of 24 h. Measurement of the $L^*a^*b^*$ values was performed using a Gretag Macbeth Spectrolino spectrophotometer (no UV filter, D50 illuminant, 2° observer) with an aperture of 4 mm. These measurement conditions are specified in ISO 18946:2011; the D50 illuminant is commonly used in graphics arts applications. Each swatch was measured three times to provide the mean $L^*a^*b^*$ values. Measurements were also taken for a control set which did not undergo any treatment. Colorimetric computation of the measured values was then performed to obtain the average ΔE for each sample, as per ISO 18946:2011.

Optical examination of the samples was also performed to provide a visual evaluation of humid bleed. Photomicrographs, typically at $\times 25$ and $\times 50$ magnifications, were captured using a Zeiss Axioskop microscope fitted with an AxioCam digital camera to assess colorant migration.

3 Results

3.1 Plain and Archival Papers

Initial results obtained for the uncoated plain paper are shown in Fig. 2. This data set includes both dye-based and pigment-based inksets. These samples were exposed to both environmental conditions.

We can make a number of observations from this data.

1. The differences between the Ave ΔE values for dye and pigment-based inks are apparent. It appears that the colour change measured for the dye-based inks is greater under both environmental conditions.
2. There is variation in the Ave ΔE values within the dye-based inksets.
3. The dye-based inks demonstrate greater colour change under the high humidity condition. The pigment inks do not appear to be preferentially susceptible to either condition.
4. The majority of colour change occurs in the first week of exposure, although there is some continued change over the following three weeks.

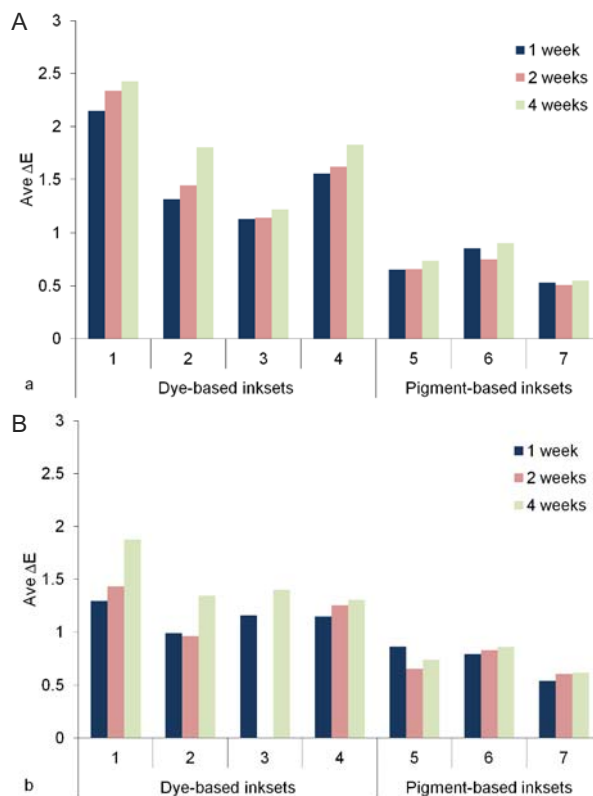


Figure 2: Plain paper exposed to a) 25 °C, 85% RH and b) 40 °C, 80% RH.

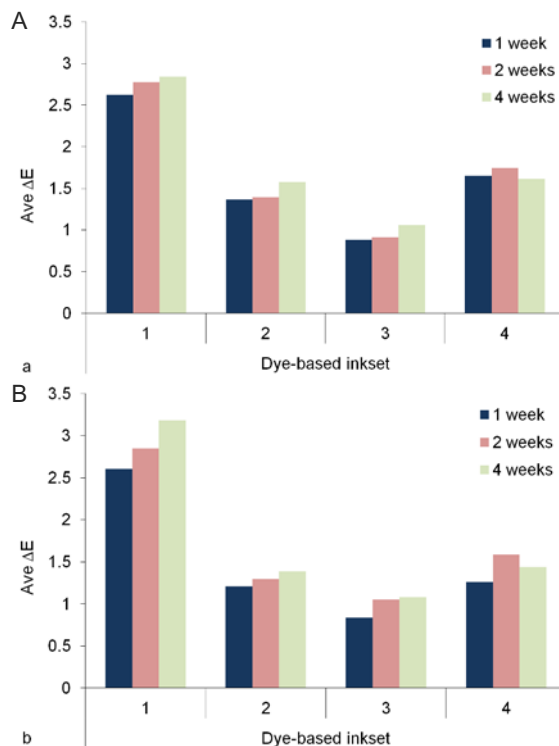


Figure 3: Archival paper exposed to a) 25 °C, 85% RH and b) 40 °C, 80% RH.

Fig. 3 shows colorimetric data from four dye-based inks printed on an archival paper. This substrate shows similar behaviour to the plain paper, but the differences between the environmental conditions are less marked. However, there is still a significant

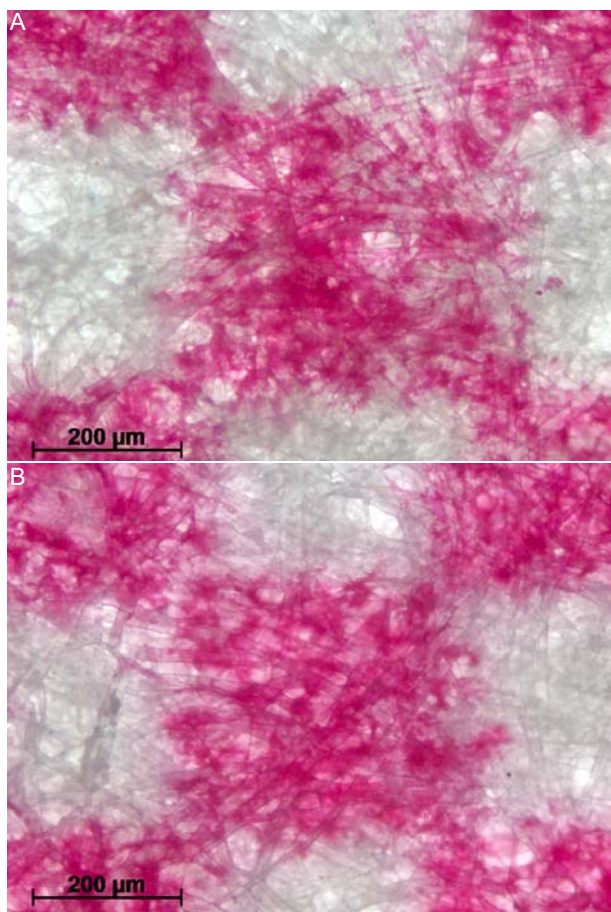


Figure 4: Micrographs showing an archival paper printed with a dye-based ink, a) unexposed and b) after 4 weeks exposure at 25 °C, 85%RH. Magnification ×100.

change in the Ave ΔE values. Micrographs of these samples allow for optical examination, as shown in Fig. 4. These micrographs show the magenta density checkerboard swatch for inkset 1 for an unexposed sample and one that had undergone 4 weeks exposure at 25 °C, 85% RH. The extent of humid bleed, though slight, can be seen in these images and is most apparent where the coloured squares intersect. These slight changes are however much more apparent in the ΔE values.

3.2 Swellable Paper

Comparison of the archival and plain paper substrates with swellable media reveals significant differences for the dye-based inksets. Fig. 5 shows the extent of humid bleed seen in two different types of swellable paper. The coating on a swellable paper consists of a water absorbing organic polymer. The coating on both these substrates is gelatin and they are two different generations of the same product: substrate B is one of the earliest swellable papers used with dye-based inks, whereas substrate A is a more recent paper.

These substrates show significantly increased values of Ave ΔE when compared to the plain and archival papers. As previously seen, the most change occurs in the first week of exposure and increases slightly

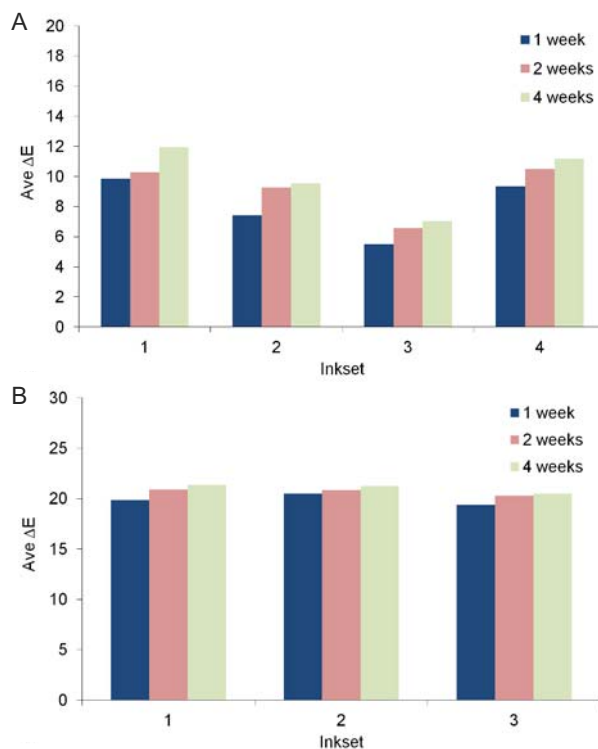


Figure 5: Colorimetric data for two different swellable papers printed with dye-based inksets and exposed to 25°C, 85%RH.

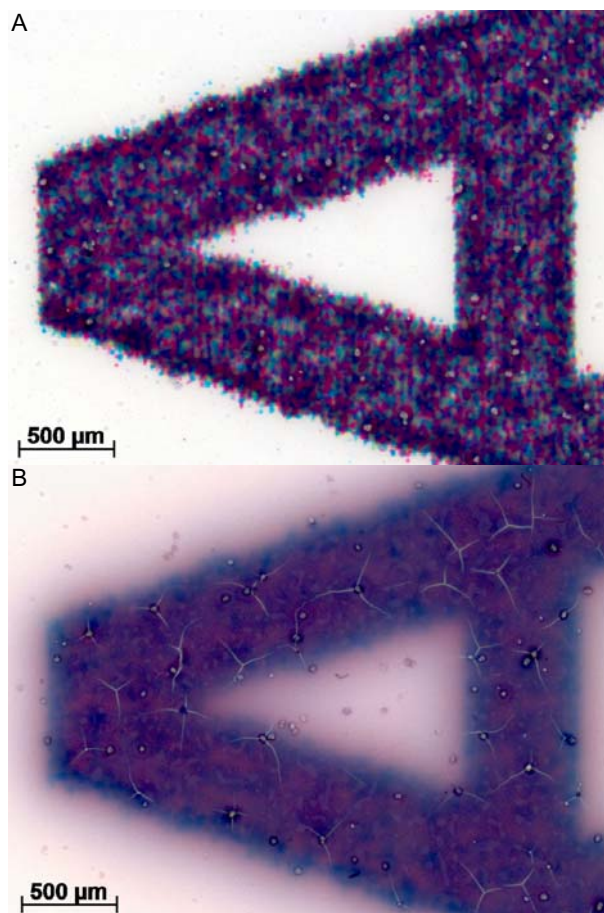


Figure 6: Micrograph showing humid bleed for swellable media printed with a dye-based ink, a) unexposed and b) after 4 weeks exposure at 25 °C, 85% RH. Magnification ×25.

with increased duration. The difference between the two generations of swellable media is also apparent.

The extent of humid bleed is obviously visible when viewed with the naked eye and severely affects the image quality of the print. Fig. 6 shows the deterioration in image quality for a dye-based ink printed on substrate A. It can be seen that there is significant bleed for at least one of the ink colours. Fig. 6b also shows the presence of small cracks in the swellable coating which appear to radiate from the centre of trapped air pockets.

This is a very severe test for swellable products as the test conditions are likely to take these through the glass transition point, that is, they cause the swellable layer to soften, which facilitates migration of soluble material through it.³ As this transition point is dependent on relative humidity, softening of the swellable layer may be seen at room temperature if the humidity is sufficiently high. This results in a change in colorant behaviour and illustrates the importance of identifying the media type - or acknowledging that this type of paper might be present in collections not well-classified to item level - when assessing display and storage conditions.¹⁰ Other media also exhibit changes in behaviour at high humidities.⁴

3.3 Microporous Paper

Fig. 7 shows a comparison between a dye and pigment-based ink (inksets 2 and 7 respectively) printed on a microporous paper and exposed to both environmental conditions. It can be seen that there is a significant difference in the values of Ave ΔE between the dye and the pigment-based inksets. The colour change for the dye-based inkset is significantly higher than that seen for either of the uncoated papers and the lateral bleed, in particular, is visible to the naked eye. However, this ink-media combination performs better than the same inkset printed on the swellable substrate (Fig. 5, inkset 2).

As seen with the plain paper substrate, it is apparent that the dye-based ink is more sensitive to both environmental conditions. Within each inkset, there is little difference between the environmental conditions, although there is a slight increase in Ave ΔE for the dye-based ink under the high humidity condition. The pigment-based ink appears to show a greater colour

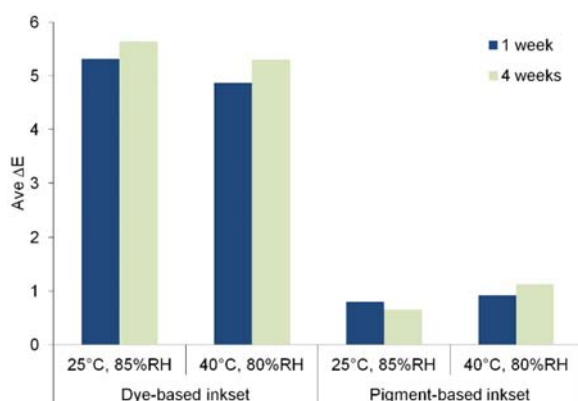


Figure 7: Comparison of dye and pigment-based inks (inksets 2 and 7 respectively) printed on microporous media for both environmental conditions.

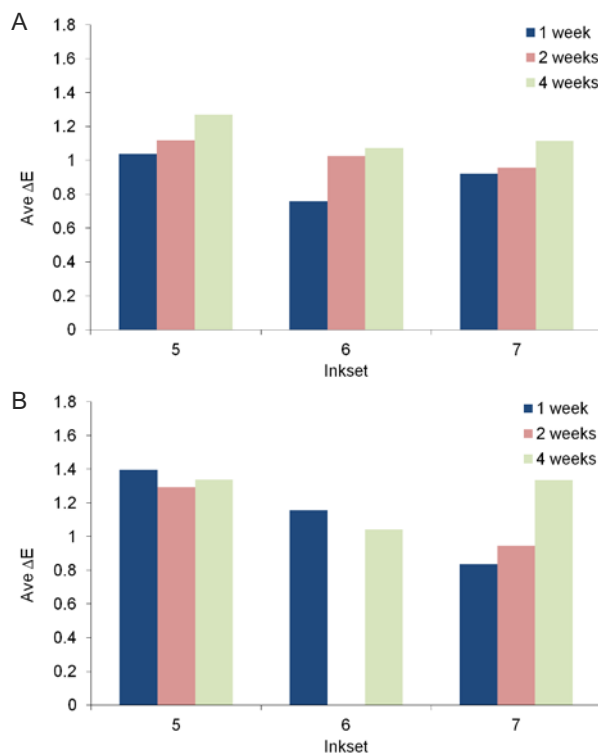


Figure 8: Colorimetric data for both microporous papers printed with the three pigment inksets and exposed to 40 °C, 80% RH.

change under the high temperature condition. However, for both inksets these differences in Ave ΔE fall within the experimental uncertainty.

Fig. 8 shows the colorimetric data for all three pigment-based inks printed on both microporous substrates and exposed to environmental conditions of 40 °C, 80% RH. Both substrates show some significant change after one week exposure, but the behaviour for substrate B is less easily defined with exposure time. It is notable that for this substrate the values of Ave ΔE do not necessarily increase with exposure time. This fluctuation is thought to be within the margins of experimental uncertainty.

4 Discussion

The work described in this paper indicates that plain and archival papers show low humid bleed in general, although dye-based inks are more susceptible to conditions of high humidity. Pigment inks are more stable than dye-based inks on all the substrates examined, although there is still some change in colour measured - and therefore observable - in realistic, albeit poor, storage conditions. This difference between the dye and pigment-based inks is particularly evident for the case where a dye-based ink is printed on a microporous substrate, as in Fig. 7, where a dye-based ink shows an Ave ΔE value of not less than 5 after 4 weeks exposure. However, it is evident from this work that the swellable media printed with a dye-based ink shows the greatest susceptibility to the highest humidities. Comparison of Figs. 5 and 7 reveals that, for inkset 2, the Ave ΔE value for swellable paper is almost twice that of the same ink printed on a microporous paper and exposed to the same conditions.

Differences in colour change were observed within inksets of the same type (i.e. dye or pigment). This is to be expected as a result of variations in the ink composition, including different colorants, co-solvents and other additives that improve jetting performance. In the case of pigmented inks, some lifting of the pigment from the surface was observed, which could contribute to the differences between inksets of this type.

The Ave ΔE measure quoted in the ISO 18946:2011 standard has been used here to gain a quantifiable measure of the extent of humid bleed for the whole test chart. In this regard it is capable of differentiating between the performance of a number of ink-media combinations for both environmental conditions. However, as detailed previously, the test chart contains various different elements including both checkerboard and solid swatches as well as areas of high and low density. Therefore individual variations in the test target swatches may be obscured when calculating an average ΔE value for the entire chart.

Visual examination of the individual swatches indicated that the extent of humid bleed varied in accordance with the colorant or colorants present in the swatch. For example, the dye-based inks generally demonstrated greater humid bleed in the magenta swatches than the cyan areas. This observation was supported by colorimetric data from the relevant checkerboard areas.

While solvents and other ink components may also affect humid bleed, the major and most obvious difference between different colours in an inkset is the dye or pigment. It is therefore logical to conclude that the colorant chemistry is a significant factor in its humidity sensitivity. The main classes of colorant used in inkjet inks include azo and phthalocyanine.

In order to obtain a deeper understanding of the effect of humidity on image bleed, it is worth considering these areas of the test chart separately. Many of the dye-based inks examined in this paper contain a pigmented black ink. Consequently it would not be expected that the black swatches and alphanumeric characters contained within the test chart and printed with such an inkset would be affected to the same extent as the dye printed swatches. An initial examination of the data indicates that, in many cases, removing all swatches with a black pigment component from the analysis of dye-based samples results in a slight increase in the Ave ΔE value. The test chart also contains unprinted areas; inspection and measurement of these swatches will provide information regarding yellowing of the substrate under humid conditions.

It should be noted that low values of Ave ΔE , such as those seen in the case of the plain paper media and microporous substrates printed with a pigmented ink, correspond to humid bleed that is not easily visible to the naked eye. To an untrained eye under standard viewing conditions (CIE D50 illuminant, 500 lux illumination),⁹ a value for ΔE^*_{ab} of 2-3 generally corresponds to a visible colour difference, but this value may be lower for grey and neutral areas. These low values of Ave ΔE will be particularly susceptible to any uncertainties inherent in the methodology.

5 Conclusions

This work provides an in-depth evaluation of the humidity sensitivity of inkjet prints, with particular reference to the behaviour demonstrated by various ink-media combinations used in the period 2000-2010. It can be seen that there are wide variations in the behaviour of different ink-media combinations, and that these variations are apparent even within inksets and media of the same type.

Only the plain paper and pigment inkset combinations showed insignificant changes. In general, pigment-based inksets are less sensitive to elevated humidity, for all paper types. All of the dye-based inksets showed measurable humid bleeding even in the room temperature range. Given the known low glass transition of the coating on many swellable papers, and in particular of earlier generations, the results of test method ISO 18946:2011 have to be understood in terms of realistic storage conditions for archival and heritage material: in many storage situations the test conditions of 40 °C and 80% RH which imply a low level of inkjet print stability could be considered relevant only to tropical climates where storage is at ambient temperature ranges. They do however highlight that one serious malfunction of air-conditioning systems, leading to elevated humidity levels, could lead to irreversible damage to such material. This acceleration of degradation with high stress conditions is the background to Arrhenius testing.¹¹

However, the results provide valuable information regarding the comparative stability of the inkjet prints studied. As dye-based inks, particularly those printed on swellable and microporous media, exhibit increased sensitivity to humidity it may be inferred that the longevity of such prints may be reduced. This, in some cases pronounced, sensitivity of inkjet prints to elevated humidity is particularly concerning in the case where the provenance and composition of a print is unknown. In these cases, simple tests may be performed to give some indication of the substrate in question: swellable papers feel slightly sticky on the printing side when touched with a lightly moist finger and also tend to retain fingerprints well. Microporous papers squeak when rubbed with a dry finger, as the coating absorbs the oils and moisture that would otherwise act as a lubricant.

The colorimetric data for all substrates indicates that the most significant change happens after only one week exposure to elevated humidity. This suggests that performing tests at shorter time scales would provide valuable information about the vulnerability of the print in the case of short term exposure, such as the failure of environmental controls.

It is also necessary to quantify the uncertainties associated with the methodology to fully evaluate the test method and outcomes. Repeat tests on ink-media combinations covered in this work will provide information regarding the reproducibility of the test procedure. In the same way, uncertainties resulting from any measurement errors may be quantified by repeating the measurement procedure for a single sample. Statistical data for duplicate ink-media prints exposed to a specified environmental condition may also be gathered.

Further work would be valuable to characterise the humidity sensitivity of inkjet prints. Detailed examination of the test chart would allow for further evaluation of the separate swatches and variations contained therein. Examination of the alphanumeric areas of the chart would aid in the assessment of the humidity sensitivity of inksets and media used for documentation purposes. The effect of residual solvent on humidity stability is also an ongoing area of investigation.

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7 References

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