STEPHANIE PORTO AND AARON N. SHUGAR

The Effectiveness of Two Cationic Fixatives in Stabilizing Water-Sensitive Dye-Based Inks on Paper

ABSTRACT

Temporary fixatives such as cyclododecane and Paraloid B-72 have long been used by paper conservators to protect water-sensitive media during aqueous treatment of paper artifacts. Recent research has focused on the application of ionic fixatives used in the textile industry to preserve modern synthetic dye-based inks on paper during aqueous deacidification. This study examines the effectiveness of two commercial ionic fixatives currently used in the paper and pulp industry, Cartafix GS and Cartafix NTC liquid fixatives, in improving the wet-fastness of inkjet ink on common office paper during immersion in a water bath. Analytical techniques used in this study include optical microscopy, spectrophotometry, and Fourier transform infrared spectroscopy (FTIR).

INTRODUCTION

Aqueous washing is an essential technique in the repertoire of the paper conservator that can often improve the stability and appearance of the paper artifact. When a conservator is faced with water-soluble inks or dyes on a paper support, the decision arises to either forego washing or to use a temporary fixative on the sensitive media in order to protect it during treatment. The choice of fixative is guided by these provisions: that it be applied easily, that it neither change the appearance of the media or the paper nor decrease their stability, that it effectively protect the media during treatment, and that it be easily removed.

Film-forming fixatives such as cyclododecane and Paraloid B-72 have long been used by paper conservators to protect water-sensitive media during aqueous treatments. Each of these materials has its pros and cons. As mentioned above, two important considerations in choosing a temporary fixative are the application and removability of the fixative. While B-72 has been known to require toxic solvents in both its

application and removal, cyclododecane has the added advantages of solvent-free application when used in the molten state, and effortless removal from the surface of the paper by gradual sublimation. Effectiveness of the cyclododecane film during aqueous treatment can, however, be variable. Due to the dimensional change differential between the film and the swelling paper fibers experienced during washing, very small cracks may result which can allow water to creep into the protected paper and cause bleeding of the media. Though suggestions have been made regarding a double application of cyclododecane on front and reverse using both pressure and heat (Brückle et al. 1999) and even an ingenious dual-layer technique using both cyclododecane and the more flexible B-72 (Muñoz-Viñas 2007), the problem with film-forming fixatives is that the fixed area remains inaccessible to water and thus does not receive the benefits of treatment. The use of butyl or propyl alcohol as a temporary water resist has also been suggested (Dwan 1998), and while this system, like cyclododecane, is also easily reversible upon evaporation, it requires extreme vigilance during treatment. The problems associated with any localized treatment also apply to the use of these temporary masks, and include possible formation of tidelines, and a difference in aging properties of the treated and untreated areas (Keynan and Eyb-Green 2000).

An alternative to film-forming fixatives like cyclododecane and B-72 is a chemical fixative that interacts with the ink on a molecular level and changes its chemical structure, rendering it insoluble in water. This type of fixative is most appropriately used with inks containing dyes of an ionic nature. If an oppositely charged ionic substance is added to the dye, the dye can be precipitated in the form of an insoluble complex. Thus, cationic fixatives will precipitate anionic dyes and anionic fixatives will precipitate cationic dyes.

CHOICE OF INK AND FIXATIVES

Past research has focused on the application of ionic fixatives used in the textile industry to preserve modern synthetic dye-based inks on paper archives during aqueous

deacidification (Bredereck and Siller-Grabenstein 1988; Leroy and Flieder 1993; Blüher et al. 1999; Hanus et al. 2004). Bredereck and Siller-Grabenstein (1988) report that most dyes used in modern inks are anionic in character. Inks which contain anionic dyes include ball point pen ink, some fountain pen inks, some stamp inks, and inkjet ink. Inkjet ink is commonly used in printing documents and photographs in the office or home and was chosen as the media to be fixed in this study. Its range of colors allows the examination of different inks containing various dyes. In addition, its ability to be applied to a paper substrate in a consistent manner by a printer made it a good choice for producing standardized samples used for testing. Since cationic fixatives are required to fix anionic dyes, cationic fixatives were chosen as the focus of this research. In past studies, cationic fixatives which showed favorable results with a variety of anionic dyes on paper included Sandofix WE, and Rewin EL (Leroy and Fleider 1993; Blüher et al. 1999). Sandofix WE, a polymer of dicyandiamide, formaldehyde and ammonium chloride, was especially successful in fixing red, blue, green and black dyes.

Due to a restructuring of the manufacturing company and changes in product line, suppliers of the above-mentioned cationic fixatives were difficult to locate. In their stead, similar fixatives currently used in the paper and pulp industry were procured. This study examines the effectiveness of two commercial cationic fixatives, Cartafix GS and Cartafix NTC liquid fixatives (available from Clariant Corporation), in improving the wet-fastness of inkjet ink on common office paper during immersion in a water bath. These products are used in the pulping process to fix dyes added to pulp in order to make colored papers. The fact that these fixatives are already used with cellulosic material such as wood pulp made them a logical choice for fixing dye-based inks on common office paper which is primarily made of wood pulp.

It should be mentioned here that a third fixative was considered for testing, Cartafix SWE, but after poor performance in initial mock-up experiments it was discarded as a possible fixative for use in conservation. These preliminary results were surprising, as this particular fixative is advertised as a polymer of dicyandiamide and was expected to produce similar results to those achieved with Sandofix WE based on its similar chemical structure. It may be that proprietary formulas are actually very different even when the listed active ingredient is the same. Also, it is possible that the textile fixatives differ in strength or action from the paper pulp fixatives.

METHODS

Preparation of Samples

Cyan, magenta, yellow, and black color swatches were printed on Boise X-9™ copy/multi-purpose paper using an HP Deskjet 6122 printer with HP Inkjet print cartridges #78 (tri-color cartridge) and #45 (black cartridge). A set of closely spaced lines printed in each color was also included with the color swatches on the samples. Printed samples were then pre-aged in a Blue M aging chamber operated at 50°C and 70% RH for approximately 20 hours. The temperature and relative humidity were chosen as a standard aging setting for multiple users. This step was taken to allow the newly printed media to bond well with the paper substrate.

At the suggestion of the product manager of the Paper Division of Clariant Corporation, a 5% aqueous solution was prepared from the concentrated Cartafix NTC and GS liquid fixatives with deionized water. Bredereck and Siller-Grabenstein (1988) mention the necessity of having a stoichiometric proportion of ions in the dye and in the fixative in order to achieve successful precipitation of the dye. However, this seemed nearly impossible to accomplish using the unknown starting concentrations of the proprietary fixatives. In their testing, Leroy and Fleider (1993) used a 10% Sandofix solution and Blüher et al. (1999) used 3–3.5% solutions, therefore a 5% concentration seemed appropriate and in keeping with previous testing of similar materials.

Fixatives were applied overall with an airbrush on a suction table to both the reverse and the front of the printed samples as Blüher et al. (1999) describe. A spray application on a suction table (as opposed to application by immersion) offers the advantage of being able to monitor any migration of the inks during the application process by inspection of the blotter beneath. The reverse was coated first so that any mobile ink would be drawn out through the front of the paper and into the underlying blotter. After allowing the applied fixative to dry under suction, the front was also sprayed and allowed to dry under suction. The fixed samples were allowed to rest in an environment of around 20°C and 50% RH for 3 days before immersion washing was undertaken.

Washing of the samples was done in separate baths of 20°C deionized water adjusted to pH 7 with calcium hydroxide. Samples were first humidified by misting with water in order to allow even wetting during washing. The samples were then immersed for 25 minutes, then removed from the bath and placed on blotters, and finally transferred to screens to be air dried.

The following samples were prepared: a control sample (C) which was not treated beyond initial pre-aging, one that was fixed with Cartafix GS and not washed (GS), one that was fixed with Cartafix NTC and not washed (NTC), one that was fixed with Cartafix GS and washed (GS-W) one that was fixed with Cartafix NTC and washed (NTC-W) and a sample that was washed without being fixed (W). Another set of samples was prepared in the same way and reserved for future accelerated aging.

Monitoring Color Change and Ink Migration

A GretagMacbeth Color-Eye spectrophotometer was used to make color measurements of each color swatch (cyan,

	GS	GS-W	NTC	NTC-W
Paper	**2.58**	**2.89**	0.60	0.67
Cyan	**2.50**	**2.14**	**3.55**[†]	**3.72**[†]
Magenta	**1.75**	**1.77**	**14.18**[†]	**12.60**[†]
Yellow	0.83	0.80	**19.16**[†]	**18.76**[†]
Black	1.05	1.00	**3.99**[†]	**2.90**

	GS-W	NTC-W
Paper	**4.37**[†]	**3.63**[†]
Cyan	**4.22**[†]	**7.63**[†]
Magenta	**2.87**	**20.61**[†]
Yellow	**2.95**	**25.21**[†]
Black	**1.93**	**4.87**[†]

Figs. 1–2. Total color difference (ΔE⋆) observed after fixing (left). Total color difference (ΔE⋆) observed after washing (right)

 Numbers in bold indicate "noticeable" color difference, which is defined as ΔE⋆>1.6. A dagger ([†]) indicates "unacceptable" color difference, which is defined as ΔE⋆>3.2 (Michalski and Dignard 1997)

magenta, yellow and black) as well as of the paper substrate on prepared samples before and after fixing and after washing. A 2mm area was measured at a 10° observer angle, using the D65 illuminant and the CIELAB color space.

A Zeiss Axio Imager reflected light microscope was used to monitor lateral bleeding of the inkjet inks in the printed black lines included on the samples. Because the black lines are actually a mixture of cyan, magenta, yellow, and black inks, changes in all four inks could be observed at once. Photomicrographs were taken of the same pair of lines on representative samples at 50X magnification before and after fixing and after washing.

Cross sections of the black swatches on representative samples were also prepared in order to compare the depth of ink penetration into the paper substrate. Cross sections were cut with a sharp razor blade and soft-mounted into metal clips for viewing on the microscope. Traditional mounting in epoxy resin was avoided as solubility of the inkjet inks in the resin could present problems. Photomicrographs were taken of the cross sections at 200X magnification.

FTIR Analysis of Ink and Fixatives

The infrared spectra of the fixatives and the cyan, magenta, yellow and black inkjet inks were collected using a Continuum microscope (Thermo Spectra Tech) coupled to a Magna 560 FTIR spectrometer (Nicolet). Samples were applied to MirrIR glass slides and placed in a desiccator for two weeks to remove any water content. Spectra were collected by transflection and were compared to a reference library of spectra in order to determine the chemical makeup of the fixatives and the inks.

RESULTS

Colorimetric Analysis

L⋆a⋆b⋆ values of the color swatches and the paper substrate were recorded before and after fixing of the samples,

and after washing. The total change in color (ΔE⋆) of the swatches was calculated by the spectrophotometer software. This data is presented in figures 1 and 2. While a conservation treatment would never consist of fixing without washing, color measurements were taken after fixing in order to quantify the amount of ink migration which may have occurred during application of the fixative.

Optical Microscopy

After the application of Cartafix GS, it was noted that the colored inks lost some of their saturation and bled somewhat. After washing, the colors appeared more neutral and faded. The black ink, however, remained intact. A comparison of photomicrographs taken before and after fixing with Cartafix GS and after washing offers a sense of the amount of bleeding/fading that occurred in the ink (fig. 3). After fixing with Cartafix NTC, it was found that the magenta ink clearly bled and faded, while the yellow ink all but disappeared. The remaining cyan ink also showed evidence of bleeding. The dark black ink dots, however, retained their original appearance. After washing, there was almost no magenta left on the sample, and the cyan ink was a mere shadow of its former self (fig. 4). After washing, an unfixed sample appeared completely devoid of magenta, cyan and yellow. Again the black ink remained in place on the paper substrate, without any noticeable color change (fig. 5).

Photomicrographs of cross sections taken from the black color swatch on representative samples were used to examine the penetration of the inkjet ink into the paper substrate before and after fixing and after washing. Four to five measurements on each cross section were averaged to find the mean ink depth. These values are listed in figure 6. While the control sample showed a distinct layer of ink about 23 microns deep, the sample fixed with Cartafix GS demonstrated that the inks had been pulled further into the paper substrate, with the magenta ink staining the paper fibers. The cross section of the sample fixed with Cartafix NTC revealed
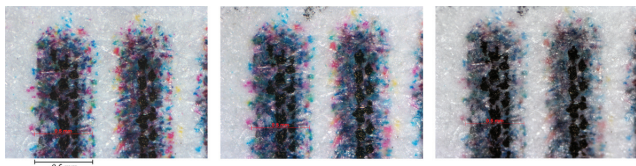
Fig. 3. Photomicrographs of printed black lines before (left) and after (center) fixing with Cartafix GS, and after immersion washing (right). Note the very slight bleeding of colored inks after fixing and slight fading after washing, while the black ink remained intact

Fig. 4. Photomicrographs of printed black lines before (left) and after (center) fixing with Cartafix NTC, and after immersion washing (right). Note the marked bleeding and fading of colored inks after fixing and further fading after washing, while the black ink remained in place
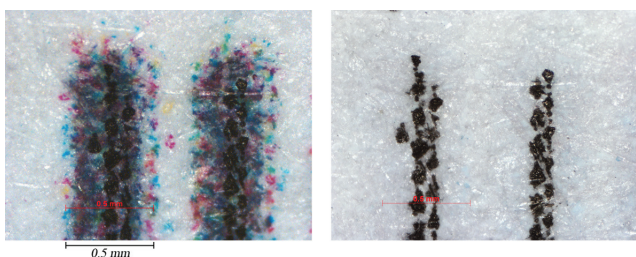

Fig. 5. Photomicrographs of unfixed printed black lines before (left) and after (right) immersion washing. Note the complete disappearance of colored inks and the stability of the black ink

Sample	Mean Ink Depth (µm)
C	23.40
GS	31.64
GS-W	45.28
NTC	22.47
NTC-W	24.25
W	32.32

Fig. 6. Mean ink depth on representative samples, in microns

how the inks had bled such that discrete ink spots were no longer very apparent. Migration of the magenta ink further into the paper substrate had also occurred, leaving the cyan ink as the dominant color at the surface of the paper. The cross section of the washed sample illustrated the stability of

the black ink, as it was still visible on the surface of the paper as distinct dark spots. Remnants of colored inks, however, were difficult to find. Interestingly, the paper substrate of the unfixed washed sample had a slightly dull or grayed appearance, most likely caused by staining of the fibers with a mixture of the soluble colored inks. UV fluorescence microscopy was attempted, but no fluorescence of the inks was noted.

FTIR Analysis

Spectra of the inks collected by FTIR (fig. 7) were complex and impossible to identify by comparison to a reference library. The spectra were all consistent, however, with a material that most likely contains a number of components including a binder, a synthetic organic dye, a humectant, a surfactant, and a biocide.

Spectra of the fixatives (fig. 8) also failed to produce matches with known reference spectra available in the library. A few insights were gained, however, by examination of the spectra. The presence of a sharp peak at around 2200 cm^{-1} in the spectrum of Cartafix GS indicates the C≡N stretching of a cyano group, while characteristic peaks around 1630 cm^{-1} and 3200 cm^{-1} point to an amide group.

DISCUSSION

Before an interpretation of colorimetric data is presented, a few words should be said about the state of current color-measuring technology. Ongoing research continues in the search for better color difference equations which more accurately match human perception of color difference (Berns 2000). Some of these newer equations are being used in current research, however, a familiarity with the color equation based on the L★a★b★ color space [$\Delta E^\star = I (\Delta L^\star)^2 + (\Delta a^\star)^2 + (\Delta b^\star)^2 I^{1/2}$] supports its continued use. Michalski and Dignard (1997) offer color quality standards based on $\Delta E^\star$ in their research on the appearance change of powdery paint after consolidation. They define "noticeable" color change as a total color change greater than 1.6, while a "just perceptible" color difference is reported between 0.25–0.5 $\Delta E^\star$ units. An "unacceptable" color difference is characterized by $\Delta E^\star$ greater than 3.2. These thresholds are adopted in this study in order to qualify the numerical color data produced by the spectrophotometer.

Colorimetric analysis of fixed samples shows that a noticeable color change resulted in almost all color swatches after application of both Cartafix GS and Cartafix NTC. Cartafix NTC generally effected much more drastic color changes than Cartafix GS, with unacceptable change in the magenta and yellow color swatches. The examination of cross sections taken from representative samples also revealed the migration of colored ink into the paper substrate during fixing, which was most likely the result of fixative application to the front of the samples while under suction. Photomicrographs of the
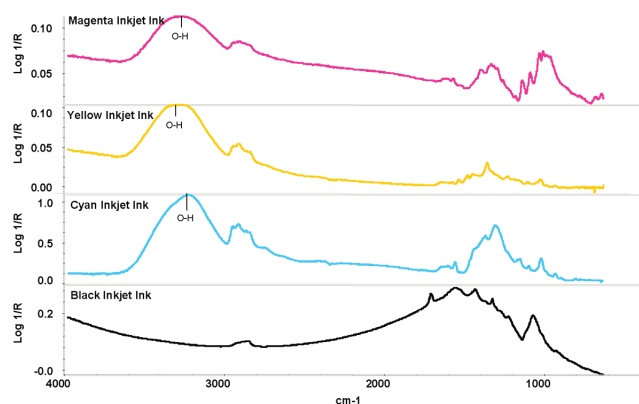
Fig. 7. FTIR spectra of HP inkjet inks. Note the absence of an O-H stretch in the spectrum of the black ink
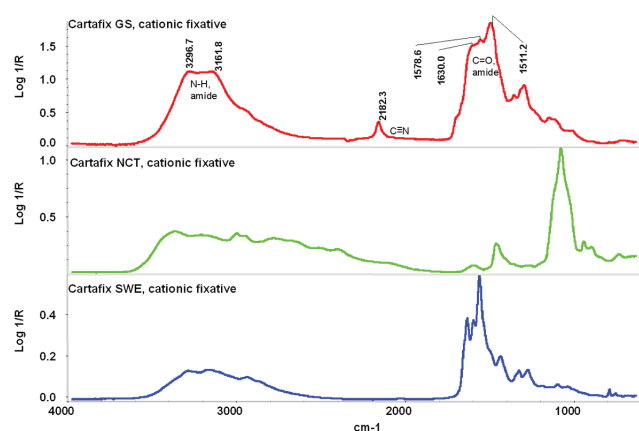

Fig. 8. FTIR spectra of Cartafix cationic fixatives. Note the characteristic peaks of amide and cyano groups in the spectrum of Cartafix GS

fixed samples (figs. 4–5) provide visual evidence to support the colorimetric data, while images of the unfixed sample before and after washing (fig. 5) illustrate exactly how water-soluble the colored inks are. The cyan, magenta and yellow inks appear to be totally fugitive, while the black ink appears quite stable. This suggests that the black ink may have a very different composition from the colored inks. It is quite possible that the black colorant is a pigment rather than dye, or that a water-insoluble binder such as wax or resin is used.

FTIR analysis of the inks supports the observation that the colored inks are fundamentally different in composition from the black ink. The absence of the large O-H stretch in the FTIR spectrum of the black ink could be evidence that its binder lacks the hydrogen-bonding functional groups which make the other colored inks so water-soluble (fig. 7). FTIR analysis may also provide some explanation for the more successful fixing characteristics of Cartafix GS. Evidence of cyano and amide functional groups in the FTIR spectrum for Cartafix GS suggests that this fixative, like Sandofix WE, may

be a derivative of dicyandiamide (fig. 8). This could account for its generally better performance as a fixative for the inkjet inks. Interestingly, the lack of a cyano group in the spectrum for Cartafix SWE brings into question Clariant Corporation's description of this particular fixative as a dicyandiamide. This misrepresentation could explain why Cartafix SWE did not perform on par with Sandofix WE, as was expected, whereas Cartafix GS demonstrated the best fixing results.

In the bigger picture, results show that the inkjet inks were not entirely fixed by the application of Cartafix GS and Cartafix NTC. The question remains, however, whether the inks are partially soluble after fixing because of other water-soluble components of the ink, such as a possible gum binder, or because of a failure of the dye-fixative complex. It was hoped that FTIR spectra of the inks would shed some light on their composition, including the type of dye and possible binder; however, reference spectra did not provide conclusive matches. In order to choose an appropriate fixative for a modern ink, it is imperative to know the exact composition of the ink. Research by Goode et al. (2007) into the chemistry of ballpoint pen ink is a step in the right direction.

FUTURE WORK

As previously mentioned, a second set of samples was prepared and reserved for eventual accelerated aging. Future work will include tracking color changes induced during an appropriate regimen of accelerated aging. Tensile testing of treated and untreated aged samples would also shed some light on the fixative's long term effect on the strength of the paper substrate.

Further research using samples printed on a variety of papers would be helpful since inkjet inks adhere differently to different papers. As McCormick-Goodhart and Wilhelm (2000) note, the stability of inkjet prints depends on both components of the printing system: the type of ink and the type of paper.

Also, an in-depth exploration of the effect of fixative concentration on successful fixation of dye-based inks is necessary, as the experimental concentration chosen for this study was based on concentrations used with other proprietary products mentioned in the literature and not on actual testing of the materials used in the study. In addition, characterization of the inkjet inks using a combination of microchemical tests and chromatographic techniques would aid in understanding their composition. Isolation of the dye colorant from the other components in the ink may allow better examination of the extent to which the fixative complexes with the dye. Experiments using the fixatives in conjunction with one another may also prove useful, as various dye molecules present in the inks will react differently with the various cations in the fixatives. For example, if one fixative is particularly successful in fixing the cyan colorant and another in

fixing magenta, then a mixture of the two fixatives may offer more complete fixation of multi-colored inks.

CONCLUSION

Based on this study, cationic fixatives used in the paper and pulp industry do not appear to be as effective in protecting inkjet inks on paper during aqueous treatments as was originally hoped. While both Cartafix GS and Cartafix NTC did improve the wet-fastness of the ink when compared with the unfixed sample, the amount of bleeding and fading which resulted after washing would be considered objectionable when performing an actual conservation treatment. In the case of Cartafix NTC, application of the fixative alone was enough to cause substantial migration of the ink resulting in unacceptable color change. Better fixation of the media may be achieved if more is known about the exact composition of the fixatives and the dye-based inkjet inks, including the chemical structures of the active cation in the fixative and the anionic dye molecules in the ink.

In conclusion, even if further research of commercially available ionic fixatives finds products that will successfully stabilize certain dye-based inks on paper, the use of ionic fixatives in conservation will be a matter of personal judgment. Since the inks are permanently changed by interaction with the ionic fixative, their use goes against the notion of reversibility, which is often a key factor when considering conservation treatment. While a suitable ionic fixative should not change the appearance of the ink, it does change its chemical structure. This brings up questions regarding the preservation of art historical information present in an artist's materials. If an artist used inks with certain known characteristics, including solubility in water, is it ethical to change those characteristics? Understandably, treatments which preserve the appearance of a material but change its chemical composition are met with skepticism by some conservators. While such treatments may be practically applicable, they may not be considered ethically acceptable.

SOURCE OF MATERIALS

Clariant Corporation
4000 Monroe Road
Charlotte, NC 28205
704–331–7000
www.clariant.us

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STEPHANIE PORTO
Masters Candidate
Buffalo State College
Buffalo, New York
sporto@cogeco.ca

AARON N. SHUGAR
Assistant Professor in Conservation Science
Buffalo State College
Buffalo, New York
shugaran@buffalostate.edu