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Ionic Fixatives for Water-Sensitive Media

INTRODUCTION

Originally an industrial product used in textile and paper dyeing processes, ionic fixatives were introduced in paper conservation in the 1980s with the intent of preserving the legibility of dye-based inscriptions during aqueous treatment of archival and library materials (Bredereck and Siller-Grabenstein 1988).

Ionic fixatives can form almost water-insoluble complexes with oppositely charged dyes. Although ionic fixatives can be far more effective in fixing dye-based inks that are otherwise hardly fixable with conventional film-forming fixatives, they also present potential problems. Ionic fixatives may change the hue and saturation of the ink, fix paper discoloration itself, cause uneven washing of paper if applied locally, and leave chemical residue behind (the side effects of which are largely unrecorded). A recent scientific study revealed that the Bückeburg fixative solution may cause not only undesirable paper discoloration but also cellulose damage, especially in the current operational method of omitting a rinsing step (Roller et al. 2015). The same study showed that the ionic charge of the paper is changed through ionic fixative treatment.

This study explores various ionic fixatives that are currently available in the U.S., compares them for their effectiveness and aging characteristics, and finds a selection of fixatives causing relatively fewer side effects. The limitation of this study is that all test results were evaluated only by visual examination before and after aging without any molecular level analysis of the cellulose. Therefore, it is suggested to limit the application of the findings of this study only to circumstances where the benefit of using them outweighs the potential side effects, and when the application area is small enough to avoid possible weakening of the paper.

Thirteen different fixatives were gathered for this study. Twelve of them were obtained from Archroma (a branch of Clariant) and BASF between 2013 and 2015, and one of them (the mixture of Mesitol NBS and Rewin EL) was obtained from Neschen in the early 2000s. Given the possible impact of shelf life, test results with the Neschen fixative should come with a disclaimer. The fixatives tested and their basic characteristics are summarized in the Appendix.

ACCELERATED AGING TESTS

Each fixative was diluted to 5% in deionized water (except the Neschen fixative, which was used without dilution) and, using a cotton swab, was applied in an approximately 1 in. diameter circular shape onto four strips of Whatman filter paper #1. The samples were then left to air-dry. One strip was kept as a control sample, one was aged in an accelerated aging chamber without washing, one was washed for 15 minutes and set aside without accelerated aging, and one was washed for 15 minutes and then aged in the chamber. The accelerated aging condition was set for 70°C and 50%RH for 96 days. After aging, the samples were examined side by side, under normal light and under UV light.

When examined under normal light (fig. 1), the unwashed samples developed noticeable discolorations after accelerated aging with three fixatives: Cassofix FRN-300, Catiofast 2345, and Nylofixan HF. When washed, with the exception of Nylofixan HF, most of the fixatives performed well, causing little to no noticeable discoloration in the paper before and after aging. The areas marked in dotted rectangular boxes in figure 1 indicate fixatives that developed visible discoloration.

Examination under UV light showed remarkable florescence patterns (fig. 2). The areas marked in dotted rectangular boxes in figure 2 indicate the fixatives that developed noticeable fluorescence. All fixatives tested showed innate fluorescence in varying degrees from faint to moderate as shown in the control samples. When these fixatives were aged without washing, the fluorescence of each intensified. However, the sample washed for 15 minutes showed an overall decrease in fluorescence compared to the control, indicating that the washing process was effective in rinsing out fixatives from the paper. However, when the washed samples were aged, a slight remnant of fluorescence remaining after washing notably intensified, even in those areas that appeared clear after washing. The only fixatives that did not

Presented at the Book and Paper Group Session, AIC's 45th Annual Meeting, May 28-June 2, 2017, Chicago, Illinois

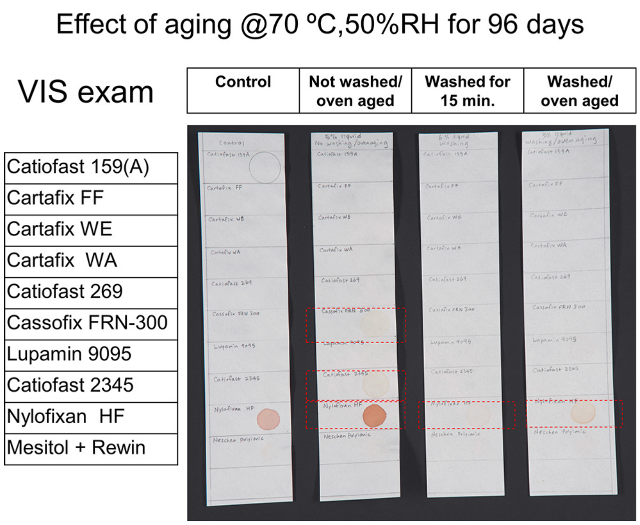

Fig. 1. Effect of aging at 70°C and 50%RH for 96 days, examined under visible light. The red dotted rectangular boxes in the picture indicate where visible discoloration developed.

develop noticeable florescence after aging were Cartafix FF and Catiofast 2345. When tested on actual media, Catiofast 2345 was found to be not effective as a fixative, dispersing any writing media in contact. Therefore, Cartafix FF stood out as being superior to other fixatives in this study in terms of causing the least amount of visible discoloration and UV fluorescence after aging.

In comparison, Cartafix WE showed slight but noticeable UV fluorescence development after accelerated aging. Cartafix WE is synonymous with Sandofix WE. Sandofix WE has been tested extensively (Leroy and Flieder 1993), showing that it did not damage cellulose nor adversely affect colors as long as the samples were sufficiently washed and deacidified. Therefore, it could be inferred that UV fluorescence developed after aging in this study might not necessarily mean that damage had occurred to the cellulose. Observing the degree of fluorescence is only a qualitative tool to gauge the effectiveness of rinsing out these fixatives from paper.

The suspension solution of Mesitol NBS and Rewin EL, also known as the Neschen fixative or Bückeburg fixative, did not perform well in this study, leaving fluorescing residue before and after aging. Mesitol NBS and Rewin EL have been actively used since 1997 as a part of the Bückeburg process. A recent study stated that Rewin EL was the main cause of cellulose damage, but Mesitol NBS did not seem to have any negative effect on cellulose (Roller et al. 2015).

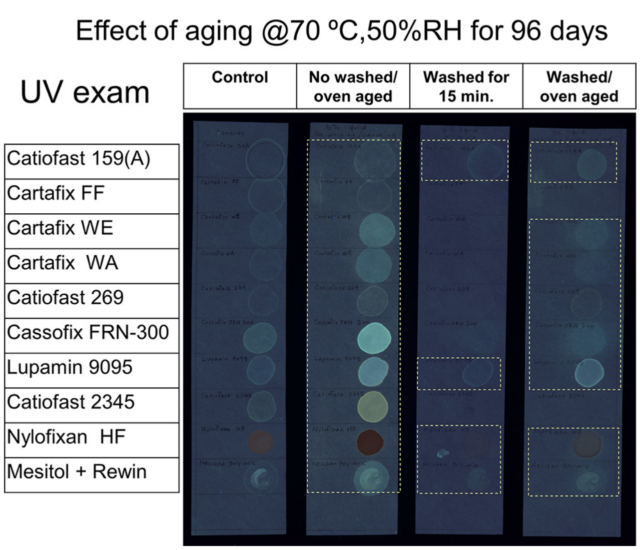

Fig. 2. Effect of aging at 70°C and 50%RH for 96 days, examined under UV light. The white dotted rectangular boxes indicate where noticeable fluorescence developed. UV photo credit: Richard Caspole, Yale Center for British Art.

APPLICATION METHODS

In various published articles on ionic fixatives (Brederick and Siller-Grabenstein 1988; Leroy and Flieder 1993; Blüher et al. 1999; Havlínová et al. 2005; Porto and Shugar 2008), reaction time given for different fixatives varied from 1 to 15 minutes, and the concentration of the fixative used varied from 1.2% to 30%. In this study, all experiments were performed with a 5% concentration both in a solution and in a gel mixture, and the reaction time was approximately 1 to 2 minutes.

When a paper sample was treated overall with an ionic fixative, it was preferable to wash the paper before the fixative completely dried, resulting in less fixative residue left in the paper. The effect of a drying step between the fixative application and washing steps was observed under UV light, which showed that slightly more fluorescing residue remained in the paper if the fixative was allowed to dry on the paper before the washing step.

However, confining the applied fixative only to the media area seemed necessary when applying ionic fixatives to localized areas in heavily discolored paper. Ionic fixatives could fix the paper discoloration itself and cause uneven washing between fixed and unfixed areas. One way to achieve a precise application to a localized area was to apply a fixative solution using a small brush on a suction platen while drying the applied solution with a hair dryer.

Another way to achieve a precise application was to apply the fixative in a mixture with methylcellulose A4M gel. A gel-mixed fixative helped minimize sinking and bleeding of the media during fixative application, especially for the extremely sensitive writing inks, such as felt-tip pen inks and fountain pen inks. A gel-mixed fixative was applied first on the front with a small brush over a suction platen and then on the verso without a suction platen. Subsequently, the object was immersed in a bath for washing. The gel was then gently brushed off in the bath during washing, approximately 1 to 2 minutes after putting the object in the bath. It was observed

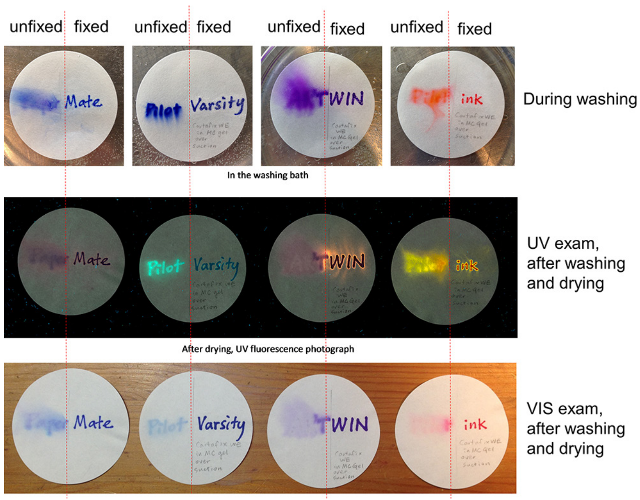

Fig. 3. During and after treatment. Four different pens applied on Whatman filter paper were locally fixed with Cartafix WE 5% concentration mixed in 4% methylcellulose A4M gel applied on the front and the back, and washed in a bath by immersion. Brightly colored fluorescing components in the writing media were partially mobilized during washing, visible under UV light. UV photo: Richard Caspole, Yale Center for British Art.

that if the gel-mixed fixatives were left on the media for too long without washing, the poultice action of the gel would compete with the fixative action; therefore, it was preferable to wash the paper shortly after the fixative gel was applied.

TESTING ON COMMERCIAL PENS AND INKS

Different ionic fixatives mixed with methylcellulose A4M gel were tested on commercial felt-tip pens and fountain pens applied on Whatman filter paper #1. After fixing and immersion washing, the treated samples were examined under visible and UV light (figs. 3, 4). Most of the cationic fixatives worked well preserving the legibility of the pen markings, but not without unavoidable minor changes and losses in color. Some cationic fixatives were slightly better than others in terms of fixing ability. Two anionic fixatives (Appretan N 92100 and Catiofast 2345) and one cationic fixative (Lupamin 9095) failed in action.

Three brands of commercial liquid ink were also tested: Winsor & Newton calligraphy ink for fountain and dip pens, labeled as nonwaterproof and lightfast; Dr. Ph. Martin's Bombay India ink, labeled as waterproof and pigmented; and Higgins dye-based drawing ink, labeled as transparent washes. Blue, green, red, and purple colors were tested for each brand. Each color was applied to Whatman filter paper #1 and air-dried. Each sample was then soaked with a 5% solution of each fixative and washed on a wet blotter to visualize any movement of the ink (fig. 5). The treated samples were organized in groups: control, not fixed and washed, fixed and washed giving acceptable results, and fixed and washed giving unacceptable results (fig. 6). All cationic fixatives performed well for Winsor & Newton calligraphy inks and Dr. Ph. Martin's India inks. Two anionic fixatives, Catiofast 2345 and Appretan N 92100, failed in action. Interestingly, the Higgins dye-based drawing inks could not be fixed by any of the cationic or anionic fixatives tested, suggesting that some components other than the dyes in the inks may inhibit fixative action.

OUTLOOK

Several factors should be considered when deciding to use ionic fixatives. Ionic fixatives permanently alter the composition of the media and the ionic character of paper. Some

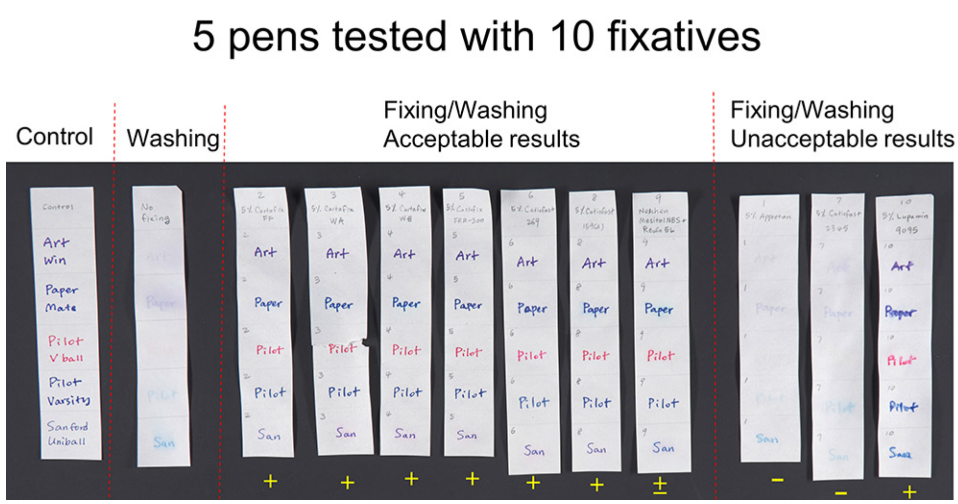

Fig. 4. After treatment. Five different pens applied on Whatman filter paper were locally fixed with 10 different fixatives mixed in methylcellulose A4M gel and then washed in a bath by immersion. The paper strips from left to right indicate control, washed without fixing, washed after fixing with Cartafix FF (+), Cartafix WA (+), Cartafix WE (+), Cassofix FRN-300 (+), Catiofast 269 (+), Catiofast 159(A) (+), a mixture of Mesitol NBS and Rewin EL (– and +), Appretan N 92100 (–), Catiofast 2345 (–), and Lupamin 9095 (+). The plus (+) and minus (–) signs below the paper strips indicate the ion charges of each fixative.

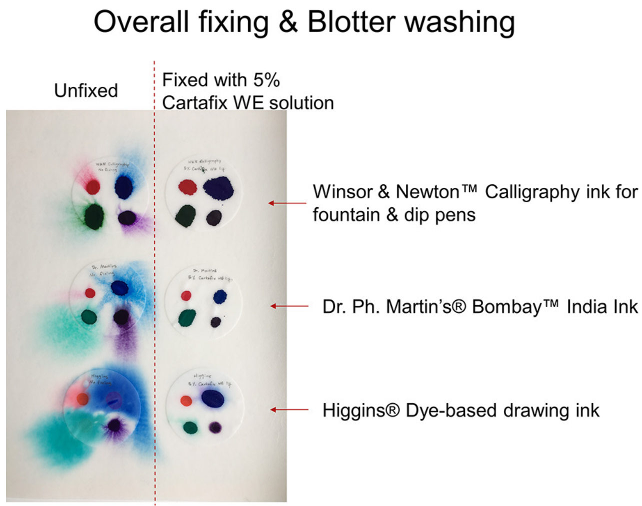

Fig. 5. During treatment. Three different brands of ink applied on Whatman filter paper were fixed overall with Cartafix WE 5% solution and then washed on wet blotter.

degree of change in the hue and saturation of color may occur. Long-term effects on cellulose molecules have not been sufficiently investigated in most of the fixatives mentioned earlier. Sufficiently rinsing the fixative from the object after application is important to minimize possible long-term side effects.

Based on this study, although limited to visual examination only, the author cautiously suggests Cartafix FF, a cationic fixative, as a viable fixative, potentially better than the other tested fixatives in this study, because it developed the least amount of fluorescing residue in the paper after accelerated aging, and it effectively fixed all of the tested media comparably or better than other tested fixatives.

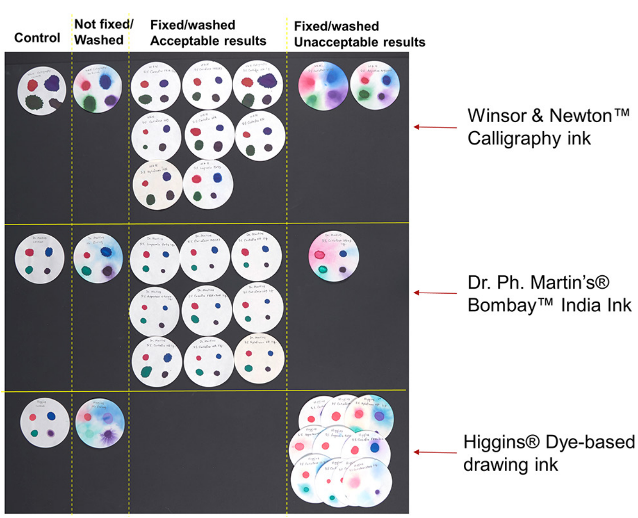

Fig. 6. After treatment. Three different brand inks applied on Whatman filter paper were fixed overall with 10 different fixative solutions and then washed on wet blotter.

Cartafix WE, a cationic fixative synonymous with Sandofix WE, developed slight fluorescence after aging in this study. However, a detailed previous study by Leroy and Flieder (1993) showed that Sandofix WE did not cause cellulose damage or adversely affect the colors. Cartafix WE was versatile to all media tested in this study and therefore may be another viable cationic fixative.

The author could not acquire any effective anionic fixatives for this study. Therefore, the author refers to the recent study by Roller et al. (2015) about the positive properties of Mesitol NBS.

The choice of 5% concentration in all tests in this study could be unnecessarily high. Under lower concentration, a few more fixatives might have shown more promising results in terms of discoloration and fluorescing residues after aging.

ACKNOWLEDGMENTS

I appreciate the generosity of Archroma/Clariant, BASF, and Neschen for providing fixative samples for this study. I would like to thank Dr. Paul Whitmore, Dr. Catherine Stephens, and Dr. Jens Stenger, Institute for the Preservation of Cultural Heritage, Yale University, for providing valuable advice and help with the accelerated aging processes; Professor Joan Irving, Winterthur/University of Delaware Program in Art Conservation, for allowing me to share my experiences with her students; Professor Dr. Irene Brückle, Stuttgart State Academy of Art & Design, for having given me the motivation to study this topic; and Debora Mayer, Helen H. Glaser Conservator, Harvard Weissman Preservation Center, and her staff for giving me the opportunity to share my experience and receive valuable feedback.

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Porto, S., and A. N. Shugar. 2008. The effectiveness of two cationic fixatives in stabilizing water-sensitive dye-based inks on paper. *Book and Paper Group Annual* 27: 63-69.

Roller, J., A. Pataki, A. Potthast, and I. Brückle. 2015. Aqueous washing treatment aids: How to remove ionic fixatives from paper. *Restaurator* 36 (4): 307-331.

SOURCES OF MATERIALS

Archroma US Inc. (paper and textile division of Clariant)
4000 Monroe Rd.
Charlotte, NC 28205
704-331-7000

BASF Corporation
11501 Steele Creek Rd.
Charlotte, NC 28273
800-346-8590

GSK mbH (previously Neschen)
http://www.gsk-conservation.de/en_index.html

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APPENDIX

Fixing Agents

Name (company)	Ion charge	Chemical information
Suspension of 1.2% Mesitol NBS & 6% Rewin EL (Neschen)	Mix of anionic and cationic	Mesitol NBS: anionic fixative, methylene-linked condensation product of arylsulphonic acids and hydroxyaryl sulphone; brownish powder or brownish liquid Rewin EL: cationic fixative, nitrogen-containing condensation product with formaldehyde
Appretan N 92100 (Archroma/Clariant)	Anionic	Acrylic ester copolymers in aqueous dispersion; self-crosslinking; a coating/binder that is applied on top of dyes/pigments; acts as a barrier to water by cross-linking
Cartafix FF (Archroma/Clariant)	Cationic	Fully condensed polyamine resin; a highly effective cationic colorant fixative in producing colorfast colored tissue, napkin, and toweling grades
Cartafix SWE (Archroma/Clariant)	Cationic	Guanidine, cyano-, polymer with 1,2-ethanediamine, N-(2-aminoethyl)-, hydrochloride salt; auxiliary for the paper and paperboard industry
Cartafix WA (Archroma/Clariant)	Cationic	Cationic methylene guanidine; guanidine, cyano-, polymer with ammonium chloride and formaldehyde
Cartafix WE (Archroma/Clariant)	Cationic	Synonyms for Sandofix WE; methylolamide cationic fixative; textile auxiliary fixing agents; auxiliary for the paper industry
Cassofix FRN-300 (Archroma/Clariant)	Cationic	Amino aldehyde condensate; textile auxiliary chemical; improves colorfastness of cotton, rayon, and blends with synthetic fibers dyed with direct, acid, and reactive dyestuffs
Nylofixan HF (Archroma/Clariant)	Anionic	Anionic arylsulphonate polymer in solution; a fixative used as a posttreatment to dyeing and printing on polyamide fibers and their blends
Catiofast 159(A) (BASF)	Cationic	Polyamine solution polymer; a cationic fixative and deposit control aid for the manufacture of fine paper, newsprint, mechanical specialties, and paperboard grades
Catiofast 269 (BASF)	Cationic	Poly(polydiallyldimethylammonium chloride) liquid solution; a cationic fixative and deposit control aid for the manufacture of fine paper, newsprint, mechanical specialties and paperboard grades
Catiofast 2345 (BASF)	Anionic	Polyacrylate polymer solution; a deposit control aid for the manufacture of fine paper, newsprint, mechanical specialties, and paperboard grades
Lupamin 9095 (BASF)	Cationic	Copolymer of vinylformamide/vinylamine in an aqueous solution
Polymin PR 971 L (BASF)	Cationic	Water-soluble, high molecular weight polyethylenimine; retention and drainage aid for the manufacture of all paper and board grades; fixing agent for fillers, fines, pitch (wood and white), anionic and nonionic colloids, pigment dyes, and direct dyes