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Does Paper with Iron-Gall Ink Corrosion Benefit from Nanocellulose-Phytate Treatment?

INTRODUCTION

Iron gall inks have been among the most common writing materials for centuries. Often, due to their mixture and complex chemistry, these inks cause ink corrosion—a complex degradation process of cellulose in the paper (Wunderlich 1994; Díaz Hidalgo et al. 2018). The ink components (iron[II] sulfate and acids), usually present in excess, catalyze two major degradation processes that usually occur simultaneously: (1) the high acid content causes hydrolytic degradation of the cellulose, and (2) free iron(II) and iron(III) ions trigger oxidative degradation of cellulose (mainly radical reactions). Damage to the cellulose chains at the molecular level alters the mechanical properties of the paper. It loses its mechanical strength and becomes fragile, but also brittle. Two processes are necessary as effective measures against ink corrosion: deacidification to neutralize the acids and inactivation of free transition metal ions (i.e., their complexation [iron(II) and iron(III) ions]). There are various approaches and protocols to chemically treat manuscripts damaged by ink corrosion (Haberditzl 1999; Dekle and Haude 2008; Albro et al. 2008; Sistach, Marín, and Garcia 2017). However, chemical treatment is only one aspect of an effective conservation process for manuscripts damaged by ink corrosion. Due to endogenous damage to cellulose, ink corrosion is often accompanied by severe mechanical damage, such as cracks, fractures, and breakouts. This requires additional physical stabilization of the paper. Depending on the extent of the damage, this is done with Japanese paper, either locally or as a full-surface lamination (Titus et al. 2009; Jacobi et al. 2011; Rouchon et al. 2012; Pataki-Hundt and Walter 2018).

Various types of nanoscale celluloses are of interest as novel stabilizing materials for paper due to their close structural relationship to cellulose fibers. For this reason, there is increasing research on the application of nanocellulose in the field of paper conservation. There are different types of nanocellulose: bacterial nanocellulose, nanocrystalline, or nanofibrillated cellulose (Klemm et al. 2011; Dufresne 2018). This research focused on the use of nanofibrillated cellulose or cellulose nano fibrils (CNF). It is produced in top-down processes from pulp. In this process, the cellulose fibers are defibrillated by mechanical and chemical treatment steps, ideally exposing the elementary fibrils without shortening them. The material is obtained as a white fiber suspension with a high water content and a relatively low solids content.

Several approaches are being researched for use in paper conservation. One is to use them as dried films with adhesive to stabilize mechanical damage (Dreyfuss-Deseigne 2017). However, they can be applied directly as an aqueous suspension and stabilize the paper without the additional use of an adhesive (Okayama et al. 2016; Völkel et al. 2017). The reason is that the production of fibrils with diameters in the nanometer range and lengths in the micrometer range creates large fiber surfaces that enable strong interactions with substances from the environment. This makes a significant difference between plant cellulose and nanocellulose, which are otherwise identical at the molecular level, and leads to specific properties of the material. One can take advantage of these specific properties when using nanocellulose for stabilization. Due to the large surface area and hydrophilic properties, stabilization and attachment of CNF fibrils occur mainly via hydrogen bonds. Thus, damaged or vulnerable areas can be stabilized by the network formation without the need for an additional adhesive (Völkel et al. 2017).

Based on these positive results for stabilization of mechanical damage, the low optical interference of the objects, and their favorable aging behavior (Nechyporchuk et al. 2018; Völkel et al. 2017), the idea arose to stabilize manuscripts damaged by iron gall ink with CNF. In addition, the aim was to test whether the chemical and mechanical stabilization of papers could be combined. The stabilization with CNF was directly integrated into the calcium phytate/calcium hydrogen carbonate treatment process, and the results on the integrability were evaluated.

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DISCUSSION

Calcium phytate/calcium hydrogen carbonate treatment was chosen as the chemical treatment method because its efficacy has been proven at the endogenous level (Potthast, Henniges, and Banik 2008; Henniges et al. 2008; Henniges and Potthast 2008), and there is an effective, standardized treatment procedure (Huhsmann and Hähner 2008). The first project objective was to evaluate integrability according to the following criteria:

- Treatability and effective mechanical stabilization with CNF within the calcium phytate/calcium carbonate method, as well as preservation of the chemical efficiency of the process;
- Stabilization without intermediate drying, since intermediate drying leads to permanent changes in the material and aging properties, which has a negative effect on the object;
- Avoidance of migration processes of the metal transition ions, which can be induced by the renewed influence of humidity.

The standard treatment protocol of calcium phytate/calcium hydrogen carbonate treatment, according to Huhsmann and Hähner (2008), includes five steps. CNF was integrated into this treatment process either by adding the CNF to the treatment baths or by applying the CNF as an additional treatment step before or after chemical stabilization (fig. 1).

The sample material used was rag paper from a handwritten collection of sermons from 1839 and 1840. The condition of the ink corresponded to condition rating 2 (Reißland and Hofenk de Graaff 2001). The optical, haptic, and endogenous treatment results were evaluated before and after artificial aging (in a closed system at 80°C and 75% humidity for 10 days) (TAPPI 2003).

The following section presents the main results of the combined treatment. For a more detailed account of the treatments and analyses and a broader discussion of the results, the reader should refer to "Combining Phytate Treatment and Nanocellulose Stabilization for Mitigating Iron Gall Ink Damage in Historic Papers" (Völkel, Prohaska, and Potthast 2020).

Visual and Haptic Results

After CNF treatment, manuscripts show no to minor visible changes. Influencing factors are the amount of CNF applied and the color of the paper or ink, as the CNF layer tends to be perceived as whitish on darker substrates. Due to the homogeneous distribution on the surface, the writing of the manuscript is only slightly affected. In addition, no fibrous structures are visible on the lettering, as is the case with Japanese paper, which is particularly positive for readability on densely written papers.

In a CIELab measurement, the color changes of the unaged and aged samples in the form of yellowing could be compared and quantified. Here, ΔE (Euclidean distance) represents the average color change and is calculated from the change in brightness and the color gradients (International

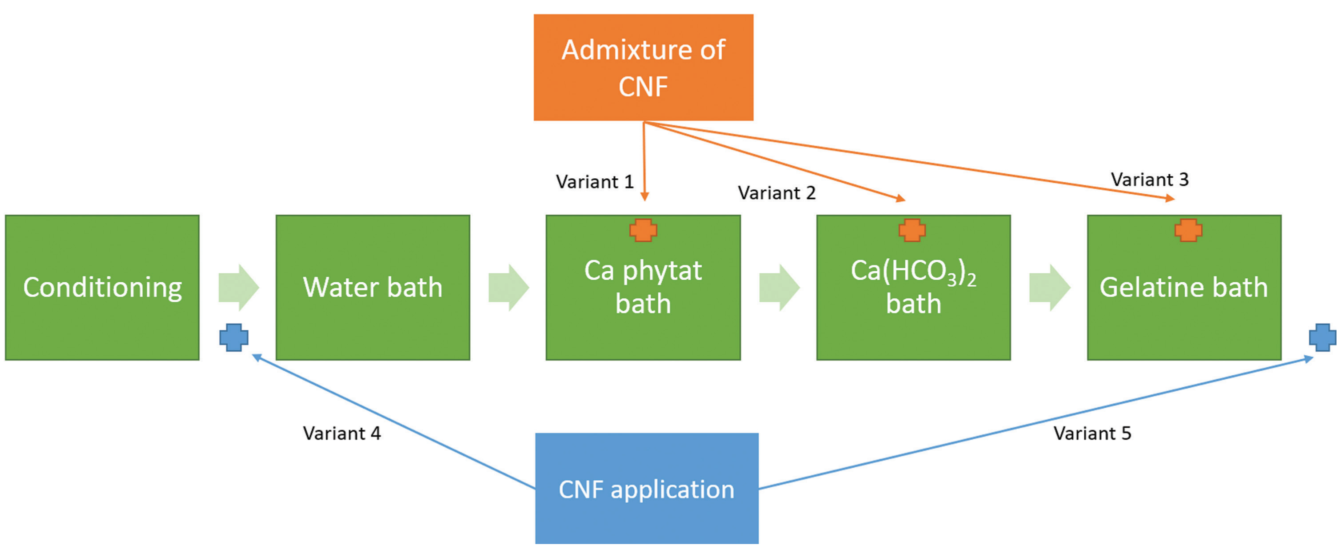

Fig. 1. The application of CNF was integrated into the calcium phytate/calcium hydrogen carbonate treatment at various stages. Either it was added to the treatment solutions as an additive (Variants 1–3) or it was integrated as a separate treatment step (Variants 4 and 5).

Commission on Illumination [CIE] 2020). The untreated references show high color changes (ΔE ↑) and are clearly yellowed (fig. 2). For the treated reference, the yellowing has been significantly reduced by the chemical treatment (ΔE ↓). The same is true for the treated samples combined with CNF phytate (fig. 2). The CIELab values are comparable to those of the treated reference, so the optical integrity of the samples is not affected by CNF.

The haptic properties are also slightly affected as a function of the application amount. No changes in thickness or flexibility were observed in the treated samples. No stresses occurred in the paper, and the paper structure remained visible.

Microscopic Results

The microscopic results are closely related to the individual treatment process that is carried out. Generally, there is a stabilizing layer on the surface of all samples, which also settles in the pore structure and covers the paper fibers. At the same time, the paper fibers remain visible under the fibril network. It was interesting to observe that in the samples, the CNF network formed both in the ink region (fig. 3, green arrows) and on the blank paper. In the backscattered electron (BSE) image, a piece of a writing loop can be seen as the ink region. In the secondary electron (SE) image, this region is also homogeneously coated with CNF, as is the blank paper area. Accordingly, the network formation was not disturbed by the different areas of the surface. A contact angle measurement showed similar and rather hydrophobic surface properties in all areas—ink and blank paper. This result was also obtained for the samples treated in Variant 5, in which the CNF was applied first, and then the chemical treatment was carried out. It can be deduced that the formation of a closed, stabilizing CNF layer is supported despite the hydrophobic surfaces. This is mainly due to the conditioning and gentle prewetting with decreasing alcohol content. Van der Waals interactions likely played a crucial role in the formation and adhesion of the CNF network.

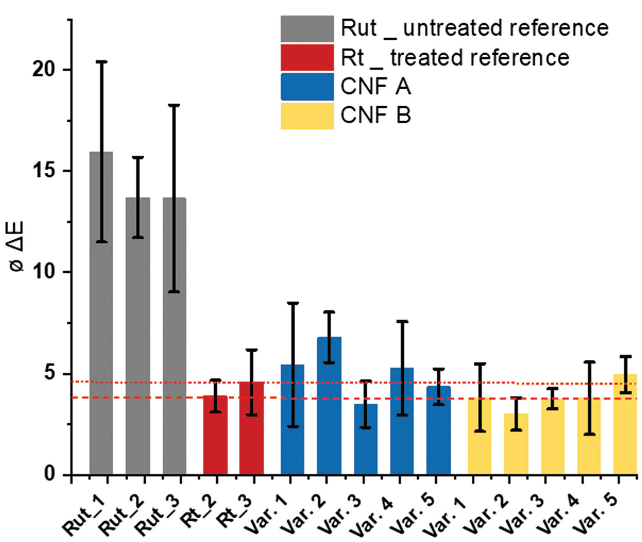

Fig. 2. Results of the CIELab analysis according to EN ISO 11664-4—sample yellowing was effectively reduced by phytate treatment. Therefore, the ΔE values are used as reference values for evaluation (dashed lines).

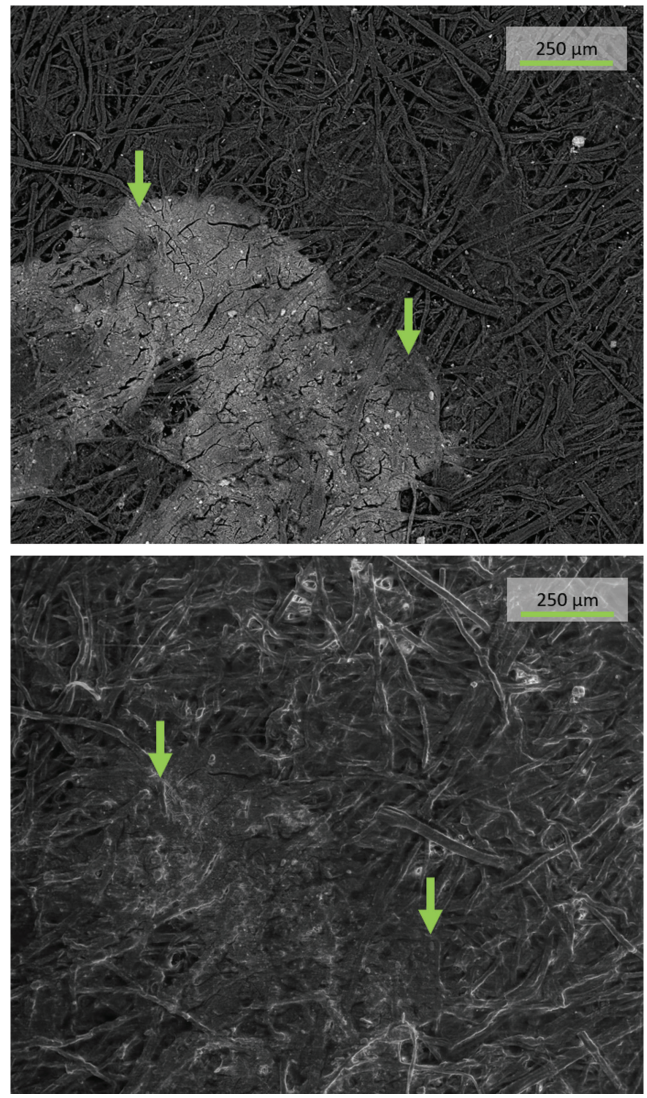

Fig. 3. The CNF forms a homogeneous layer regardless of whether the area is written on with ink (green arrows mark writing loop) or whether it is pure paper. In the BSE image (top, 150×), the ink areas and the blank paper areas can be clearly distinguished. In the SE image (bottom, 150×), everything is evenly covered with a CNF layer.

Specific results are obtained with respect to the accumulation or distribution of solution components, such as calcium phytate or calcium carbonate particles on the surface. In

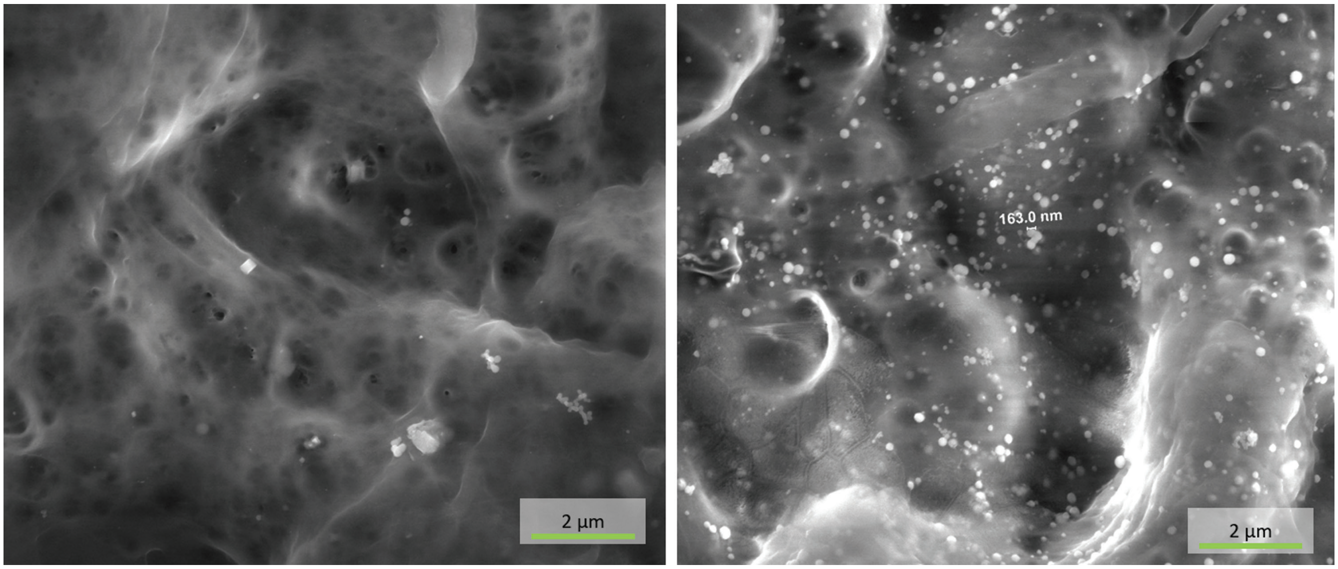

Fig. 4. Different treatment procedures produce individual results with regard to the CNF network. Comparing the samples of Variant 4 (*left*) and Variant 5 (*right*), the different degrees of enrichment of the components of the treatment solutions are apparent. In Variant 4 (*left*), the CNF network is formed as the last step, which is why only a few particles can be seen on the surface. In contrast, Variant 5 (*right*) has many particles deposited on the surface, as the CNF network is formed before the chemical treatment. These are calcium and phosphorus particles.

Variant 4, the CNF is applied as the last step, and the fibril network is formed on the surface after chemical treatment. There are only a few crystals on the surface, presumably introduced by transfer (fig. 4). In comparison, Variant 5 shows small, white crystals homogeneously distributed on the surface. They have a size between 100 and 200 nm, and energy dispersive x-ray spectroscopy (EDX) analysis determined calcium and phosphorus in the crystals. Considering that in Variant 5 the CNF is applied as the first step after conditioning, the stabilizing fibril network is already formed on the surface before chemical treatment. Within the treatment baths, calcium phytate and calcium carbonate attach to the network (fig. 4). In further analyses, no negative side effects due to these crystals could be determined.

Integrity of Cellulose

To evaluate the effectiveness of the chemical treatment with integrated stabilization, the cellulose was analyzed at the endogenous level. The molar mass and carbonyl group content were determined before and after aging using size exclusion chromatography with multiangle light scattering. These are key factors to describe the changes in the material and to evaluate the effectiveness of a new treatment. To make a meaningful comparison, the number of cellulose chain cleavages after accelerated degradation was calculated from the mean molar mass (Potthast and Ahn 2017). This allows data evaluation independent of the initial molar mass of the historical papers, which differ slightly within a sheet due to sample inhomogeneities.

After aging, all untreated reference papers showed a high number of chain cleavages (approximately 0.76) and an increase in carbonyl groups by an average of 34.5% (fig. 5). There was significant degradation of cellulose during accelerated aging without treatment measures. The results of the treated reference samples demonstrate the effectiveness of

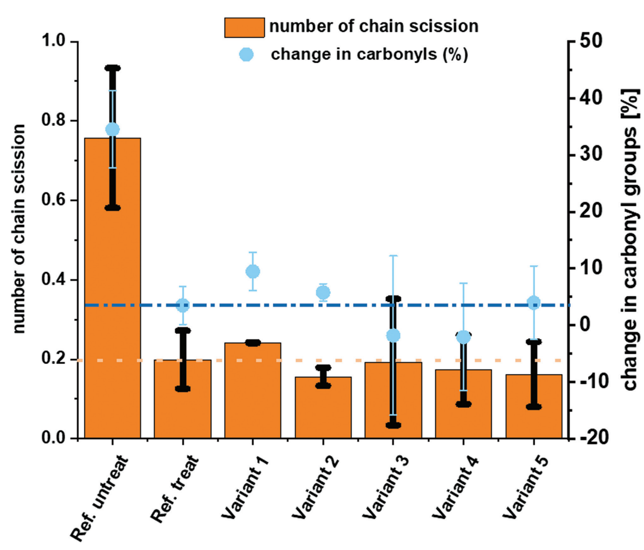

Fig. 5. Average number of chain scissions and carbonyl group contents of reference and treated samples after accelerated aging. Lines indicate average numbers from the reference treatment with phytate only.

the calcium phytate/calcium hydrogen carbonate treatment performed. As expected, both hydrolysis and oxidation were significantly slowed down. The chemical treatment reduced the number of chain cleavages to 0.20 and the formation of carbonyl groups to 3.5%. The data were used as a reference for the combination treatments. In these, it can be seen that no increased cellulose degradation occurred in four out of the five treatment variants. Treatment variants 2 through 5 behaved like the regular phytate treatment in terms of cellulose protection; efficacy was fully maintained, even when CNF was used. An exception was Variant 1, which showed a slightly increased number of chain cleavages and an increased formation of carbonyl groups. This can be attributed to the lack of a complexation bath and the shortened treatment time. The sole application of the calcium phytate/CNF suspension could not effectively mask all the iron ions.

Migration of Iron Ions

For the treatment of ink corrosion, it is always important for conservators to know how the treatment affects the migration properties of free metal ions. Therefore, the influence of additional CNF application at different stages was investigated using laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS). The measurement method is a powerful analytical tool for monitoring the spatial movements of chemical elements and showing their distribution on the paper surface. For the selected samples, the laser was passed over the ink lines at two positions each. The untreated reference showed no migration before (fig. 6) and also after aging. This can be seen in the clear and abrupt increases or decreases in iron intensity that match the ink line. Migration would be noticeable by a wider iron distribution next to the original inks.

These distinct iron profiles corresponding to the ink lines were similarly observed in the samples treated with CNF application. In the example shown (Variant 5), no broader distribution was observed in the paper either before (fig. 6) or after aging. This confirms that no water-induced migration of iron ions occurred due to the additional application. This was also found for the other variants.

Transfer Tests into Practice

Based on the successful verification of the combination treatment, work is currently under way on the transfer of this research result into practice—this project's second objective. The main intention here is to create a workflow for the treatment of severely damaged manuscripts of condition ratings 3 and 4 (Reißland and Hofenk de Graaff 2001). In addition to the application in the single-sheet process, the aim is to add a treatment as a batch process. The following section offers some insight into practical transfer results. The transfer tests are carried out with severely damaged manuscripts of condition ratings 3 and 4. They show mechanical damage, and the cellulose is degraded.

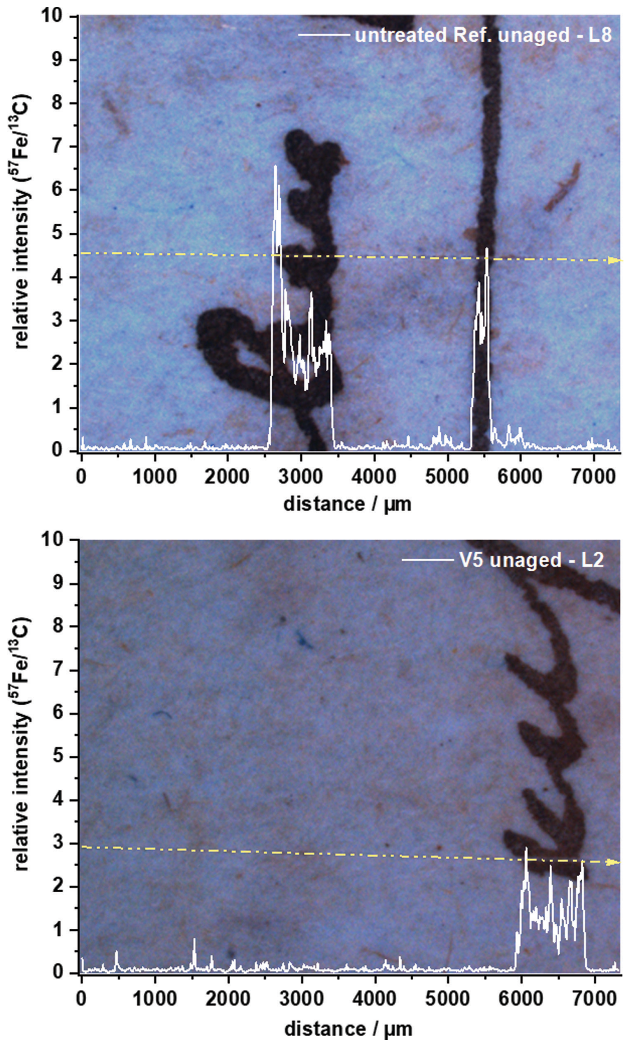

Fig. 6. No migration tendencies of the untreated reference (*top*) and the Variant 5–treated sample (*bottom*) were detected before aging. The lines visualize the course of the laser ablation.

Treatment variants 3, 4, and 5 were successfully applied to the severely damaged papers. Their workflows proved to be feasible, and they did not cause any side effects or further damage to the manuscripts.

The transfer results of Variant 4 will be presented in more detail as an example to show the possibilities and functionalities of CNF. In addition to the ink bleed-through and halos, the sample sheet showed mechanical damage in the form of breakouts and small, fine cracks in the ink lines. The treatment was carried out in a single-sheet process, and the CNF was applied as the last step.

After the chemical and mechanical stabilization treatment, the edge of the manuscript (which was also mechanically damaged due to storage and use) and the mechanical damage in the manuscript have been stabilized.

Fig. 7. Treatment Variant 4. Sample of condition rating 4 before (A) and after (B) chemical phytate treatment and mechanical stabilization by CNF. The application of CNF stabilized fine cracks, mechanical damage (C), and breakouts in the ink area (D). No further mechanical damage occurred during the treatment. Other than that, the good stabilization performance of CNF is clearly visible at the edge area and the breakouts.

The sheet itself is more stable after treatment and can be handled more easily again, as both strength and flexibility in the weakened areas have improved. Visually and haptically, CNF leaves little impression. In the ink area, it looks like a light, whitish layer, whereas in the paper area, it blends in completely and is not visually noticeable. If one recalls handwriting areas stabilized with Japanese paper, the influence due to the CNF can be assessed as low to very low.

In areas where mechanical damage has been stabilized and closed, such as ink breakouts, CNF stands out as a thin layer (fig. 7). In an image with higher magnification (10× and 150×), the film-forming properties of the CNF can be well visualized. The CNF layer forms in the paper and in the ink area. Depending on the amount and type of application, the layer closes thin cracks or fills small voids throughout.

Aspects of application optimization and treatment in higher quantities were also investigated. Unfortunately, the analytical results on the issues of transfer, optimization, and further development in the second half of the study are still pending and can only be presented later.

CONCLUSION

In the present study, a combined treatment of manuscripts damaged by ink corrosion was developed. The manuscripts can be effectively treated chemically and mechanically in a workflow of calcium phytate/calcium hydrogen carbonate treatment and CNF application. Treatment is possible in various combinations and without intermediate drying. Of the combinations reviewed, Variants 2 through 5 proved effective, whereas Variants 4 and 5 were of particular interest from a conservation science perspective. It is particularly positive that the chemical treatment penetrates and acts through the thin fibril networks. On the one hand, this allows mechanical prestabilization of severely damaged manuscripts with CNF prior to chemical treatment. On the other hand, it shows the inherent potential for re-treating of manuscripts even after stabilization with CNF.

The workflows of Variants 3, 4, and 5 could be successfully transferred to manuscripts of condition category 4. CNF acted as a stabilizing network for mechanical damage and caused only minor visual and haptic impact.

Open questions for transfer, optimization, and further development will be investigated in the second half of the study. On the one hand, this is the analytical monitoring of development and optimization tests to obtain treatment efficacy. Here, important results are currently pending, which will provide essential information for practical application. On the other hand, feasible treatment procedures are to be developed, especially for severely damaged manuscripts, which allow the treatment of several objects in addition to single-sheet treatment. Last but not least, the development of a practice-oriented workflow must always consider quality control.

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REFERENCES

Albro, Sylvia, Julie L. Biggs, Claire Dekle, Mary Elizabeth Haude, Cyntia Karnes, and Yasmeen Khan. 2008. "Developing Guidelines for Iron-Gall Ink Treatment at the Library of Congress." *The Book and Paper Group Annual* 27: 129–165.

Dekle, Claire, and Mary Elizabeth Haude. 2008. "Iron-Gall Ink Treatment at the Library of Congress: Old Manuscripts—New Tools." *The Book and Paper Group Annual* 27: 15–26.

Díaz Hidalgo, Rafael Javier, Ricardo Córdoba, Paula Nabais, Valéria Silva, Maria J. Melo, Fernando Pina, Natércia Teixeira, and Victor Freitas. 2018. "New Insights into Iron-Gall Inks Through the Use of Historically Accurate Reconstructions." *Heritage Science* 6 (1): 63.

Dreyfuss-Deseigne, Rémy. 2017. "Nanocellulose Films in Art Conservation: A New and Promising Mending Material for Translucent Paper Objects." *Journal of Paper Conservation* 18 (1): 18–29.

Dufresne, Alain. 2018. *Nanocellulose: From Nature to High Performance Tailored Materials*. 2nd ed. Berlin: Walter de Gruyter GmbH.

Haberditzl, Anna. 1999. "Tintenfraßbehandlung—Umsetzung von Theorien in Die Praxis Der Werkstätten." In *Tintenfraßschäden Und Ihre Behandlung*. Werkhefte Der Staatlichen Archivverwaltung Baden-Württemberg. Stuttgart: Kohlhammer. 221–244.

Henniges, Ute, and Antje Potthast. 2008. "Phytate Treatment of Metallo-Gallate Inks: Investigation of Its Effectiveness on Model and Historic Paper Samples." *Restaurator* 29 (4): 219–234.

Henniges, Ute, Rebecca Reibke, Gerhard Banik, Enke Huhsmann, Ulrike Hähner, Thomas Prohaska, and Antje Potthast. 2008. "Iron Gall Ink-Induced Corrosion of Cellulose: Aging, Degradation and Stabilization. Part 2: Application on Historic Sample Material." *Cellulose* 15 (6): 861–870.

Huhsmann, Enke, and Ulrike Hähner. 2008. "Work Standard for the Treatment of 18th- and 19th-Century Iron Gall Ink Documents with Calcium Phytate and Calcium Hydrogen Carbonate." *Restaurator* 29 (4): 274–319.

International Commission on Illumination (CIE). 2020. "DIN EN ISO/CIE 11664-4:2020-03, Farbmetrik_-Teil_4: CIE_1976 L*a*b* Farbraum." Berlin: Beuth Verlag GmbH.

Jacobi, Eliza, Birgit Reißland, Claire Phan Tan Luu, Bas van Velzen, and Frank Ligterink. 2011. "Rendering the Invisible Visible. Preventing Solvent-Induced Migration During Local Repairs on Iron Gall Ink." *Journal of Paper Conservation* 12 (2): 25–34.

Klemm, Dieter, Friederike Kramer, Sebastian Moritz, Tom Lindström, Mikael Ankerfors, Derek Gray, and Annie Dorris. 2011. "Nanocellulosen: Eine neue Familie naturbasierter Materialien." *Angewandte Chemie* 123 (24): 5550–5580.

Nechyporchuk, Oleksandr, Krzysztof Kolman, Alexandra Bridarolli, Marianne Odlyha, Laurent Bozec, Marta Oriola, Gema Campo-Francés, Michael Persson, Krister Holmberg, and Romain Bordes. 2018. "On the Potential of Using Nanocellulose for Consolidation of Painting Canvases." *Carbohydrate Polymers* 194 (August): 161–169.

Okayama, Takayuki, Chiemi Kadoya, Masazumi Seki, and Mao Tonoyama. 2016. "Applicability of Cellulose Nanofiber Coating Treatment for Strengthening Naturally Aged Papers." In *Pan Pacific Conference 2016: Current Research and Perspectives on Pulp, Paper and Lignocellulosic Materials*, edited by Korea Technical Association of the Pulp and Paper Industry. Seoul. 136–38.

Pataki-Hundt, Andrea, and Cosima Walter. 2018. "Comparison of Lightweight Japanese Tissues for Overall Stabilization of Documents Damaged by Iron Gall Ink Corrosion and an Alternative to Silk Screen Frames." *Restaurator* 39 (2): 109–127.

Potthast, Antje, and Kyujin Ahn. 2017. "Critical Evaluation of Approaches Toward Mass Deacidification of Paper by Dispersed Particles." *Cellulose* 24 (1): 323–332.

Potthast, Antje, Ute Henniges, and Gerhard Banik. 2008. "Iron Gall Ink-Induced Corrosion of Cellulose: Aging, Degradation and Stabilization. Part 1: Model Paper Studies." *Cellulose* 15 (6): 849–859.

Reißland, Birgit, and Judith Hofenk de Graaff. 2001. *Condition Rating for Paper Objects with Iron-Gall Ink*. ICN-Information Number 1. Amsterdam: Cultural Heritage Agency of the Netherlands.

Rouchon, Véronique, Marthes Desroches, Valéria Duplat, Marine Letouzey, and Julie Stordiau-Pallot. 2012. "Methods of Aqueous Treatments : The Last Resort for Badly Damaged Iron Gall Ink Manuscripts." *Journal of Paper Conservation* 13 (3): 7–13.

Sistach, Maria Carme, Eva Marín, and Jose Garcia. 2017. "Evaluation of Alkaline Compounds Used for Deacidification and Simultaneous Lining of Extremely Degraded Manuscripts." *Restaurator* 38 (3): 249–272.

TAPPI (Technical Association of the Pulp and Paper Industry). 2003. "Accelerated Temperature Aging of Printing and Writing Paper by Dry Oven Exposure Apparatus." TAPPI/ANSI Test Method T 573 sp-15. Atlanta: TAPPI.

Titus, Sonja, Regina Schneller, Enke Huhsmann, Ulrike Hähner, and Gerhard Banik. 2009. "Stabilising Local Areas of Loss in Iron Gall Ink Copy Documents from the Savigny Estate." *Restaurator* 30 (1-2): 16–50.

Völkel, Laura, Kyujin Ahn, Ulrike Hähner, Wolfgang Gindl-Altmutter, and Antje Potthast. 2017. "Nano Meets the Sheet: Adhesive-Free Application of Nanocellulosic Suspensions in Paper Conservation." *Heritage Science* 5 (1): 23.

Völkel, Laura, Thomas Prohaska, and Antje Potthast. 2020. "Combining Phytate Treatment and Nanocellulose Stabilization for Mitigating Iron Gall Ink Damage in Historic Papers." *Heritage Science* 8 (1): 86.

Wunderlich, Christian-Heinrich. 1994. "Geschichte Und Chemie Der Eisengallustinte: Rezepte, Reaktionen Und Schadwirkungen." *Restauro* 6: 414–421.

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