Eliza Jacobi, Birgit Reissland, Claire Phan Tan Luu, Bas van Velzen, Frank Ligterink

Rendering the Invisible Visible

Preventing Solvent-Induced Migration During Local Repairs on Iron Gall Ink

Local mending of ink-corroded areas with a water-based adhesive bears one serious risk: too much moisture transports invisible, detrimental compounds like iron(II)ions and acids out of the ink lines into surrounding paper areas, spreading ink corrosion. This process becomes perceptible just after years, therefore this risk is often underestimated. Methylcellulose, Klucel G, Gelatine, Wheat starch, Methylcellulose/Starch mixture and RepaTex® G5 were applied with three application methods: Brushing the adhesive on the paper strip before application, brushing the adhesive directly on the original through a Japanese paper, and using remoistenable tissue. The transport of components was followed by applying repairs on indicator papers with iron gall ink lines: bathophenanthroline (Fe[II]ions), Methylred (acid) and Cobaltchloride (moisture). The bathophenanthroline indicator paper successfully allowed to compare different adhesives and application techniques, visualizing the migration of iron(II) ions. All tested adhesives caused iron(II) ions to migrate out of ink lines when too much water was involved, even Klucel® G in ethanol (96 %). Applying remoistenable tissue was the only technique that provided an adhesive layer of equal thickness and allowed to limit the water content so that reproducibly good results were achieved. The indicator paper was further developed to a ready-to use product and is available on the market.

Das Unsichtbare sichtbar machen: Reduzierung der lösemittel-induzierten Migration bei Rißschließungen tintenfraßgeschädigter Papiere

Rißschließen tintenfraßgeschädigter Bereiche mit Klebstoffen auf Wasserbasis birgt ein Risiko – das Einbringen von Wasser kann unsichtbare, schädliche Verbindungen wie Eisen-(II)-Ionen und Säuren aus den Tintenlinien in angrenzende Papierbereiche transportieren und damit den Tintenfraß ausbreiten. Da dieser Prozeß erst nach Jahren sichtbar ist, wird dieses Risiko oft unterschätzt. Methylcellulose (MC), Klucel G, Gelatine, Weizenstärke, MC/Stärke und RepaTex® G5 wurden mit drei Methoden aufgebracht: Pinselauftrag auf den Japanpapierstreifen, direktes Auftragen des Klebstoffes durch das Japanpapier und Verwendung eines selbstgefertigten „Remoistenable Tissues". Der Transport löslicher Komponenten wurde sichtbar gemacht, indem auf Indikatorpapieren mit Tintenlinien gearbeitet wurde: Bathophenanthrolin (Fe-(II)-Ionen), Methylrot (Säure) und Kobaltchlorid (Feuchtigkeit). Alle Klebstoffe verursachten eine Migration von Eisen-(II)-Ionen, wenn sie zu feucht aufgetragen wurden, selbst Klucel® G in Ethanol (96 %). Remoistenable Tissues realisieren eine homogene Klebstoffschicht bei geringstmöglichem Wassereintrag und erzielten reproduzierbar gute Ergebnisse. Das Indikatorpapier erlaubt die Kontrolle und Optimierung der eigenen Arbeitsweise und ist im Fachhandel erhältlich.

For centuries iron gall ink was used for writing and drawing and therefore book and paper conservators frequently work with originals made with this ink. Iron gall ink forms a notorious problem since it might cause ink corrosion: detrimental ink ingredients affect the paper, causing depolymerisation of the cellulose chains. In saturated areas, where ink components penetrated through the paper and reached its back, the strength of the paper is usually lost, and the paper becomes critically embrittled. Mechanical stress due to bending or folding causes the formation of cracks within such ink areas. The paper breaks at random due to its low degree of polymerisation, resulting in characteristic sharp and brittle edges (Fig 1). Van Velzen classifies such decay as 'degradation tear' (Van Velzen 2006: 16). If cracks interconnect, and surround a larger area, this area may literally 'fall' out of the paper and might get lost. Such loss of material occurs when locally brittle papers are inappropriately handled on a regular basis. These objects need avoidance of further damage. If preventive measures such as supplementing the original by digital images or providing effective support measures are not applicable, paper conservators usually repair tears with water-based adhesives and Japanese paper. While this is an effective method for tear repair on paper alone, it can be harmful for paper with iron gall ink.

It is important to understand that areas with iron gall ink contain highly water-soluble components that are visible, but also invisible like iron(II) ions, sulphate ions or acids like gallic acid, which catalyse the chemical reactions responsible for the paper decay (Banik 1995: 217; Neevel 1995: 145-147; Kolar et al 2006: 182-187; Strlič et al 2006: 173-180). When those detrimental components are neither removed nor inactivated by treatment (Neevel 1995: 148; Reissland 2001: 109; Kolar et al 2006: 181-194; Lichtblau and Anders 2006: 195-214), any introduction of water is perilous. During mending with aqueous adhesives for instance, visible and invisible components migrate out of the ink into the surrounding paper in lateral and transversal direction (Rouchon 2010). Almost invisible at the moment, the decay extends to all paper areas which were wet enough to allow migration. It needs quite a long time, approxi-

1 Where ink saturated the paper, it is weak and cracks when stress is applied.

mately 25 years [1], until the decay becomes visible as discolouration, decreasing the legibility, and weakening of the infected areas (Fig 2). Therefore, the risk is often not even perceived as such.

Just recently paper conservators became aware of the problem and started to search for the most suitable adhesive (Kolbe 2004: 35; Charles 2008: 11/12; Titus 2009: 30/31; Pataki 2009: 59-63). Gelatine was suggested as best option, but still, the question remained which is the most suitable adhesive for local repairs on iron gall ink and how this adhesive should be applied. Also, would it be possible to control the amount of water introduced during mending in order to minimize unwanted long-term effects?

Iron Gall Ink and the Effect of Solvents

Iron gall ink contains a number of water-soluble products. The most detrimental are the ones catalysing the degradation of the paper fibre: iron(II) ions and acids. The ink contains different types of acids: gallic acid, tannins and hydrogensulphates. Also the presence of iron(II) and iron(III) ions contributes to the acidity. Other soluble components are Gum Arabic and, if present, dyes that were added to increase the readability of fresh ink. All these substances can, under the influence of moisture or other polar solvents, be spread out of the ink into the surrounding paper areas. Iron (II) sulphate, other sulphates, acids and gallic acid easily dissolve in water.Increasing the temperature usually improves the solubility (Rouchon et al 2008 [2]). Gallic acid is much better soluble in ethanol than in water (Schweppe 1993: 469).

Neevel and Mensch demonstrated the migration of iron and sulphur during artificial ageing with fluctuating relative humidities (Neevel and Mensch 1999: 531). While iron stayed in closer vicinity to the ink area, sulphur migrated further, in lateral and transversal direction. Helen Wilson confirmed this result and studied the migration properties under specified relative humidities [3]. She showed that at a temperature of 23 °C, a migration of Fe-ions and S-ions becomes apparent in the paper when relative humidity exceeds 65 % and becomes clearly visible at higher humidities (Wilson 2007: 67-73). To follow the iron(II) migration Wilson used a bathophenanthroline indicator (Neevel and Reissland 2005: 28-36), and applied Scanning Electron Microscopy - Energy-dispersive X-ray spectroscopy (SEM EDX) to measure the lateral transfer of iron and sulphur. Rouchon et al confirmed the lateral and also transversal migration of elements during exposure to high humidities in a humidification chamber (80-90 % RH), a Gore-Tex© Sandwich (100 % RH) and during immersion treatment in ethanol, water and water / ethanol mixtures (Rouchon et al 2009: 239). They proved that addition of ethanol to aqueous immersion treatments limited the elemental loss, but observed an enhanced formation of discoloured halos. They explained this unexpected result by a better penetration of water into the paper and the fact that insoluble components would not dissolve in the treatment solution, but migrate within the paper instead (Rouchon et al 2009: 251).

Those results were alarming. Taking into account that the enhanced humidities present during the experiments already caused spreading of soluble detrimental components out of the ink lines, direct application of water during mending, without the possibility to remove soluble components, logically would even lead to further migration. Extending the area of degradation would be the inescapable result, if the water content introduced by the mending technique could not be limited to a minimum (Fig 3).

To reduce the migration of solutes within the paper matrix, paper conservators apply particular mending techniques that limit the amount of solvent that is transferred to the original (Henry et al 1985). All involve the stabilization of the fragile area by application of a support material like Japanese paper with an adhesive.

Mending Ink Corroded Areas

Support Material

Commonly, Japanese papers of varying thickness and translucency are used as support material to reinforce cracks in ink corroded areas. Pataki (Pataki 2009: 54/55) compares the opacity of four thin tissues: RK0, 5 g/m^2, and RK00, 3,6 g/m^2 (Paper Nao), Gossamer tissue and Berlin tissue, each 2 g/m^2 (Gangolf Ulbricht). She favours the Berlin tissue since it has an 'exceptionally even structure and is very translucent' as did Titus et al (Titus et al 2009: 30).

2 Detrimental components migrated out of ink and become visible just after years.

3 During mending moisture spreads, transports invisible compounds and evaporates.

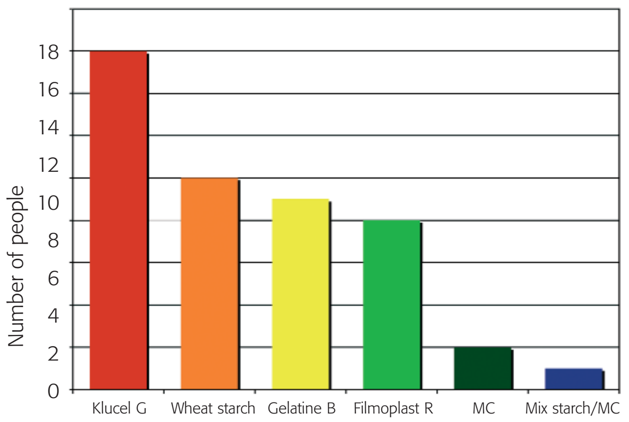
Adhesives and Ready-To-Use Products

A questionnaire sent to Dutch paper conservators revealed that for mending ink-corroded artefacts, paper conservation studios prefer different adhesives for diverse reasons [4]. Preferred are solvent-based adhesives, especially Klucel G, Wheat starch and gelatine, but also Filmoplast R, a heat-activated adhesive, is used (Fig 4; Jacobi 2009: 55). Also on the market is RepaTex® G5, a ready-to-use remoistenable tissue.

> *Klucel® G (Hydroxypropylcellulose, HPC) in Ethanol* is chosen to exclude water as solvent that might spread ink corrosion. Klucel(G solves only half of the migration problem: while iron ions and inorganic acids are hardly expected to migrate, organic acids like gallic acid and certain dyes are known to be soluble in ethanol and could spread easily from the ink into the surrounding paper. An advantage of ethanol is that it evaporates quickly, limiting the migrations duration and thus its magnitude (Ubbink and Partridge 2003: 42). The disadvantage is that, because of the quick evaporation of the ethanol, Klucel(G is usually very difficult to adhere. The adhesion is further determined by its chemical properties, having many long side and non-polar branches.

> *Wheat Starch Paste* is dissolved in water and widely used due to its excellent application properties and its known ageing properties. For mending tears in paper wheat starch paste it is a favoured choice, but for using it on already brittle ink corroded areas it is felt less useful, since it forms rather inflexible films. To improve the flexibility it is often applied as mixture with methylcellulose.

> *Methylcellulose (MC)* is regularly applied to mend ink corroded areas. Different types of MC are on the market, all can be dissolved in water. To reduce the water content, a water-ethanol mixture can be used. The viscosity of MC is an important property since it determines the necessary concentration of the adhesive applied. In her extensive study, Pataki included two types of methylcellulose with differing viscosity (MC 400 and MC 4000).



4 Dutch conservators prefer Klucel G, Wheat starch, Gelatine B and Filmoplast R for mending ink corroded artefacts.

> *A Mix of Starch Paste and MC* is suggested to use for copper corroded objects by Quandt (Quandt 2002) and was included in Pataki's tests. She recommended a mixture (starch / MC 4000) for mending ink-corroded areas (Pataki 2009: 56/57, 64).

> *Gelatine Type B (Alkali-Treated Raw Material)* has attracted a lot of international attention as an adhesive for repairs on iron gall ink in the last years (Kolbe 2001; Kolbe 2004; Nguyen 2005: 31-34; Nijhuis 2006: 18-21; Schellmann 2007: 55-66; Titus et al 2009; Pataki 2009: 64). This interest arouse as it was established that under certain circumstances some gelatine types might act as inhibiting agent for iron gall ink corrosion, since the binding qualities of gelatine may stop free iron(II)-ions to catalyse the oxidation reaction of paper fibres (Kolbe 2001: 52; Kolbe 2004: 31; Titus et al 2009: 31). However, Potthast et al (Potthast et al 2008: 858/859) could not proof the inhibiting action effect of gelatine on ink corrosion experimentally. Searching for fast and pragmatic application methods, a gelatine gel has been developed that can be used at room temperature (Charles 2008: 11/12).

> *Filmoplast R* is a ready-to-use heat-set tissue, consisting of a thin Japanese paper, which is coated with a solvent-free, heat-activated acrylic adhesive. Such thermo-activated adhesives are used to exclude any polar solvent that might spread ink corrosion, but require high temperatures above 100 °C to achieve appropriate tack. Over the years, the adhesive becomes insoluble in most solvents.

> *RepaTex® G5 Conservation Strips* are ready-to-use remoistenable tissue strips. They are made of a Japanese paper support, 5 g/m^2 (Paper Nao) with a coating of a mixture of a protein-based adhesive and methylcellulose (free of plasticizers). The adhesive is activated with water or moisture. The top layer consists of a non-woven polyester carrier, which allows better handling of the mending paper in its wetted state and is removed after drying.

Mending Techniques

> *Conventional Mending* is done by brushing the adhesive on a Japanese paper strip that is placed on a support, often blotting paper, to remove excess of solvent. The adhesive-containing paper strip is then applied onto the fragile area with tweezers and a brush. To ensure good contact, the mending paper is gently pressed down. This is the conventional technique used for mending in general (Henry et al 1985: 5). This technique cannot be used with Berlin Tissue because it is too fragile to be agitated with a brush.

> *Direct Mending* by brushing the adhesive gel directly onto the fragile area through a Japanese paper that remains as support on the degraded area (Martin et al 2011: 26/27). This technique is used to apply adhesives that are dissolved in fast-evaporating solvents (e.g. Klucel G in ethanol).

> *Preparing a 'Remoistenable Tissue'* to transfer a minimal amount of solvent (Brückle 1996; Wagner 1996; Titus et al 2009: 33-38, Pataki 2009: 52-55; van Velzen and Jacobi 2011: 36). A thin Japanese paper is coated with an adhesive film. After drying, this film can be re-activated with a very low amount ofsolvent (e.g. re-moistening when using water as solvent). Also,

water-solvent mixtures can be applied to decrease the amount of water and to shorten the drying time. With this technique, nearly transparent, extremely thin tissues can be used.

> *Using a Beat-Set Tissue like Filmoplast R* to avoid any solvent since the support paper is coated with a thermo-plastic adhesive which is activated by applying heat with a tacking iron at temperatures above 100 °C.

While those techniques aim for limiting the amount of water, the risk of migration of invisible detrimental components remains. To limit this risk, a simple monitoring technique, which allows to follow the migration of soluble, invisible components, avoiding equipment that is not available in paper conservation studios, is needed. Such a technique would allow to limit the risk of migration and to establish a mending method that is practical, quick, easy and affordable to use in the reality of a paper conservation studio.

Experimental

A cheap and easy approach that meets those requirements is the use of indicators. For the detrimental components that play a role in ink corrosion, the following indicators were chosen: bathophenanthroline indicator for iron(II) ions, methyl-red pH-indicator for acids, and cobalt chloride for water. The indicator solutions were used to prepare our own indicator papers. By applying repairs directly onto the indicator papers, the migration will become immediately visible, enabling an easy visual evaluation of the application methods and adhesives. In total, four adhesives (Methycellulose, Klucel® G, Wheat starch, Gelatine) and three methods (direct application through a Japanese paper, application on paper strips and use of remoistenable tissue) were tested that are commonly used for repairs on ink corroded artefacts. In addition, RepaTex® G5 remoistanable tissue (Gabi Kleindorfer) was included.

Preparation of the Indicator Papers

> *Bathophenanthroline Indicator Paper:* This specific indicator has no colour, but forms an intensely magenta coloured complex with iron(II) ions. Therefore, papers impregnated with Bathophenanthroline can be used as an indicator for the presence of iron (II)-ions. The indicator is very sensitive xxx (Neevel and Reissland 2005: 31; Vuori and Tse 2005: 991). For this research a filter paper (no. 1441 090, Ø 9 cm: Whatman) was impregnated with a 0.16 % solution of Bathophenanthroline ($C_{24}H_{16}N_2$ no. 133159, 500 mg: Aldrich) in ethanol anhydrous (no. 459836, 100 ml: Sigma Aldrich) by immersing it until the filter paper was saturated with the indicator fluid. The filter paper was dried in open air hanging on a rag (Fig 5).

> *Methyl Red Indicator Paper:* Methyl red (also called C.I. Acid Red 2) is an indicator dye and can be used as an acid-base indicator. Acid-base indicators do not suddenly change colour at a specific pH value. Instead, the colour change is gradual, occurring over a range of hydrogen ion concentrations. Methyl red changes colour within a pH range of 4.2 to 6.2. Under pH 4.2 it colours pink, above pH 6.2 yellow. In between its colour is orange. The Methyl-red indicator paper was made by impregnating a filter paper (no. 1441 090, Ø 9 cm: Whatman) in a 0.02 % solution of Methyl red (no. 250198, 25 g: Sigma Aldrich) in ethanol anhydrous (no. 459836, 100 ml: Sigma Aldrich) and demineralised water 60 % v/v (Fig 6).

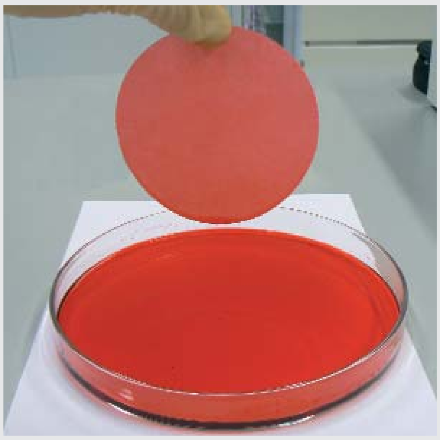
> *Cobalt (II) Chloride Indicator Paper:* Cobalt II chlorides present different colours depending on their hydratation state. Therefore, papers impregnated with cobalt (II) chloride can be used as an indicator for the presence of water. Anhydrous cobalt (II) chloride ($CoCl_2$) has a blue colour. In the presence of humidity, it turns to Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$), which has a pink colour. The change in colour is gradual: under conditions of low humidity the paper appears blue (anhydrous state), under moderate humidity the paper appears purple, and under high humidity it changes to pink (hydrate state). The indicator paper was made by impregnating filter paper (no. 1441 090, Ø 9 cm: Whatman) in a 5 % w/v solution of Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$, no. 255599, 5 g: Sigma Aldrich) in demineralised water.

Applying Iron Gall Ink on the Indicator Papers

The iron gall ink was made according to a recipe published in 'A Booke of Secrets', 1596: 550 mL red wine were warmed on a heating plate, 38 g gum Arabic (no. 63300: Kremer), 62 g gallnuts (no. 37400: Kremer), and 31 g iron (II) sulphate heptahydrate (no. 64200: Kremer) were added, all crushed into small pieces. The ink was stirred with a wooden stick, filtered through a linen cloth and filled into glass containers [5].

Two stamps made of rubber were designed and ordered to apply iron gall ink on the indicator papers (De Posthumus-

5 Drying the impregnated indicator papers.



6 Impregnating filter paper in a solution of Methyl red (to confirm).

winkel). One stamp contains 10 lines of each 1 mm broad. The space between the lines starts at 2 mm, then increases each time with 1mm. This way we could easily determine the distance of migrated compounds around the iron gall ink lines after the different treatments. The second stamp prints the inscription 'Iron Gall Ink' five times one below the other.

Preparation of Adhesives

> *Methylcellulose:* Two types of methylcellulose were used. MC2000 (Culminal MC 2000: Conservation by Design) was prepared at a concentration of 2.5 % w/v whereas MC400 (Culminal MC 400: Conservation by Design) was used at a concentration of 4 % and 8 % w/v. These adhesives were first dissolved in 25 mL hot tap water, then 75 mL of cold tap water were added and stirred thoroughly [6];

> *Hydroxypropylcellulose:* Klucel (Kluce® G: Kremer) was prepared in ethanol (96 %: Antonides) at several concentrations: 2 %, 5 % and 6 % w/v. The adhesive was first dissolved in 25 mL warm ethanol, then 75 mL ethanol were added and all stirred thoroughly;

> *Gelatine:* Gelatine (Type B, 'Restoration', Photographic grade and Technical grade: Gabi Kleindorfer) was prepared at a concentration of 3 % w/v in tap;

> *Water:* It was first left to swell over night in water at ambient temperature, then dissolved by increasing the temperature to 40oC. The solution was finally used at room temperature when it forms a cold gel as described by Charles (Charles 2008);

> *Wheat Starch Paste:* Starch (wheat starch: Peter van Ginkel) was used in a proportion of 1 part to 3 parts of water (v/v). It was prepared as paper conservators typically do in a saucier by automatic stirring for 20 min at high temperatures, 20 minutes at cooking and 20 minutes at high temperature. After heating, the paste was worked through a horsehair sieve. One part was kept and used as highly concentrated and the rest was further diluted with water.

Choice of Repair Paper

Four Japanese papers were tested: 16 g/m^2 (Kozo, RK-38: Paper Nao), 5 g/m^2 (Kozo, RK-0: Paper Nao), 3.6 g/m^2 (Kozo, RK-00: Paper Nao) and 2 g/m^2 (Mitsumata and Kozo, Berlin tissue: Gangolf Ulbricht).

Repair Techniques Applied

> *Conventional Mending:* The adhesive was brushed onto the Japanese paper. To limit the amount of transferred moisture, several techniques were tested, e.g. brushing the adhesive onto the Japanese paper, pasting it out on a non-absorbent surface, on an absorbing surface (blotting paper) or letting the solvent evaporate by holding the paper strip up for 30 seconds. The adhesive-coated Japanese paper was then applied onto the ink on the indicator paper [7].

> *Direct Mending:* The adhesives were directly brushed through a reinforcing Japanese paper (Berlin Tissue, 2 g/m^2 and Paper Nao, 9 g/m^2) onto the ink on the indicator paper.

> *Remoistenable Tissue:* Remoistenable tissues were prepared by applying an adhesive film of each adhesive onto each Japanese paper according to the method described by Brückle (Brückle 1996; van Velzen and Jacobi 2011: 36). In addition Repatex (Repatex G5: Gabi Kleindorfer) was tested. For re-activating the dry adhesive film, the following methods were applied to determine the optimal technique: using sponges of different nature as water reservoir, a felt tip pen with a water reservoir, a brush, a brush with a water reservoir, ultrasonic mist and the mist of boiling water. Then, the re-activated paper was applied onto the ink on the indicator paper.

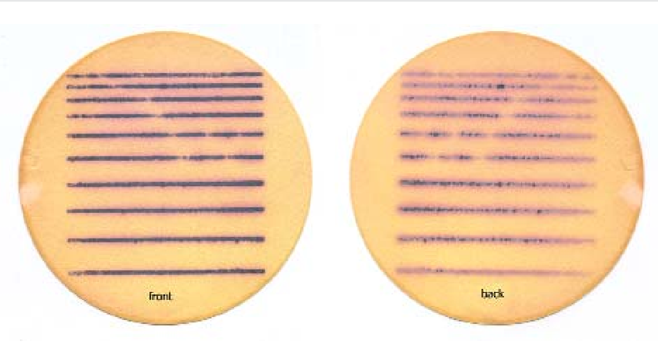
Results and Discussion

Migration after Ink Application

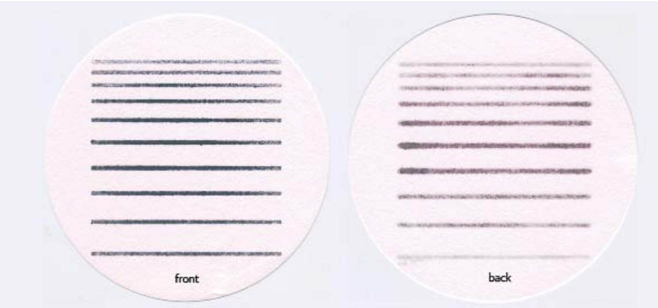
When stamping the fresh ink on the indicator papers it was observed that, when plenty of ink was applied, acids and iron(II) ions laterally and transversally spread out of the iron gall ink area into the surrounding paper (Fig 7, 8). Such spreading of ink components is typical for ink application on non-sized papers (chromatographic effect) and showed that the methyl red indicator (colour change from orange to pink) and the bathophenanthroline indicator (turning pink) both worked. The extension of migration depended on the quantity of ink applied.

However, already one hour after applying the ink, the methyl-red indicator paper turned pink. The cause of this quick change of colour remains unclear. Since we intended to examine acid migration during the repair application, the 'discoloured' methyl-red indicator papers could not be used.

The cobalt-chloride indicator paper did not give useful



7 Bathophenanthroline indicator paper: the pink colour shows the migration of iron(II) ions already during ink application.



8 Methyl red indicator paper: the pink colour shows the migration of acidic components out of the ink lines directly after ink application.

results either. After taking it out of the desiccator and applying the ink, it turned pink within minutes. This time-frame was too short to obtain reliable data on humidity distribution during a mending procedure. Indicator papers impregnated with cobalt (II) chloride change colour over a RH range of 45-55 %, which corresponded to the present RH in the atelier.

The only indicator that gave reliable results was bathophenanthroline, allowing to study the migration of iron(II) ions. Therefore, the experiment was continued with these indicator papers.

Migration Due to Direct Adhesive Application

All adhesives were applied by brush directly onto the bathophenanthroline indicator paper. An application of demineralised water was included as control. Immediately, lateral and transversal migration of iron(II) ions out of the ink lines into the surrounding paper could be observed, independent of the adhesive used (Fig 9, 10). Also, Klucel caused - less but evident - migration of iron(II) ions. This was rather unexpected. In how far the slight solubility of iron sulphate [8], the presence of 4 % of water in the Ethanol used to prepare the Klucel, or just a transport of iron(II) ions along with alcohol-soluble ink components are the cause, requires further studies. The migration of soluble components due to methylcellulose and gelatine application onto untreated papers was already demonstrated by Kolbes re-sizing experiments, showing severe discolouration after artificial ageing (Kolbe 1999: 93/94, Fig 36, 37).

Migration Due to Repairs

All adhesives were applied onto the bathophenanthroline indicator paper with the three application techniques. It was interesting to see, that all adhesives caused iron(II) ions to migrate, when applied inappropriately by transferring too much solvent. Especially starch in high and low concentration caused migration of iron(II)-ions. However, through reducing the amount of water, all adhesives could be applied in such a way that no migration of iron(II)ions was discernible.

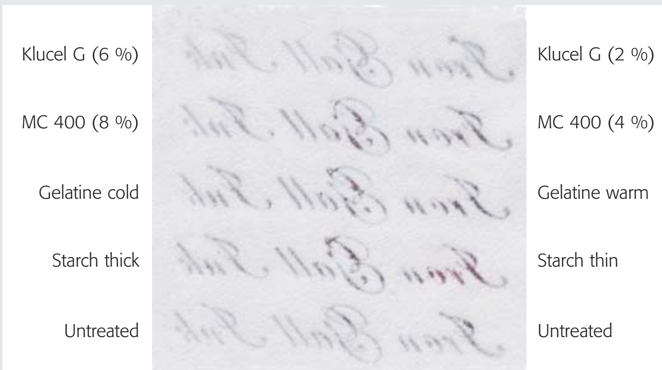
> *Conventional Mending:* In general, the results of this technique were difficult to reproduce. The distribution of brush-applied adhesive was irregular. The amount of transferred solvent remained unpredictable, varying from acceptable to non-acceptable results. Both, applying the adhesive onto a Japanese paper that lays on a blotting paper as well as holding the Japanese paper into the air for 30 seconds in order to let surplus water evaporate before applying it onto the indicator paper, gave satisfying results (Fig 11, 12). However the latter technique proved to be too slow to be applicable in real practice. Except for Klucel in ethanol (2 %), all adhesives achieved a sufficient adherence.

> *Direct Mending:* Directly brushing the adhesive through a reinforcing paper strip onto the indicator paper caused an obvious iron(II) ion migration for all adhesives, including Klucel. When applying the adhesive, a large amount of adhesive and solvent is immediately transferred onto the paper by the brush, causing a quite inhomogeneous distribution. This directly corresponded to the migration of iron(II) ions (Fig 13, 14). The

9 Iron(II) migration due to direct application of adhesives, (recto).

10 Iron(II) migration due to direct application of adhesives (verso).

11 Iron(II) migration due to conventional mending (recto).



12 Iron(II) migration due to conventional mending (verso).

adhesion achieved by Klucel was not satisfying, the paper strips could be easily removed by peeling them of.

> *Remoistenable Tissues:* The use of self-prepared remoistenable tissues proved to be the only technique leading to reproducible and satisfying results. The adhesive layer on the Japanese paper has a uniform thickness and therefore can be evenly re-activated. Again, the way how the technique is conducted determines its success. If too much solvent was transferred, a migration of iron(II) ions was visible (Fig 15, 16). For this reason, most techniques that were tested to reactivate the adhesive film on the carrier paper were not suitable. Using the steam of cooking water caused strong cockling of the paper strip and was poorly controllable. Ultrasonic mist wetted the paper strip too much, the optimal distance between mist and paper was difficult to determine. Applying moisture with a felt tip pen with a water reservoir, a brush, and a brush with a water reservoir was unsuccessful, since the amount of water transferred varied considerable and was not reproducible.

Uniform transfer of a sufficiently low amount of moisture was successful when using a kitchen-sponge cloth (cellulose, any supermarket) [9] as water reservoir. Several sponges were tested, all shared one disadvantage: their surface was too irregular, causing inhomogeneous moistening of the thin mending papers. Covering the sponge with two layers of blotting paper improved the homogeneity. For a 10 x10 cm sandwich, 30 ml of water are sufficient to transfer an equal low amount of water even during longer working periods. The water needs to be evenly distributed through the sandwich. Over time, it slowly evaporates into the air. Klucel can be successful applied as remoistenable tissue. Ethanol or Ethanol-water mixtures evaporate too fast from the sandwich when treating a larger amount of objects. Instead, Klucel can be re-activated with water.

The remoistenable tissue is kept onto the polyester film until use. The repair can be cut on the polyester film into the exact form needed. After application, repairs should not be pushed with a bone folder or other equipment, because the applied pressure might transfer moisture into the original paper. Instead, the repair paper can be positioned with a non sticking synthetic material, such as Bondina or Reemay.

Repatex remoistenable tissue did cause serious migration, since the synthetic carrier absorbs too much water, which is difficult to control and is transferred onto the artefact during application (Fig 17).

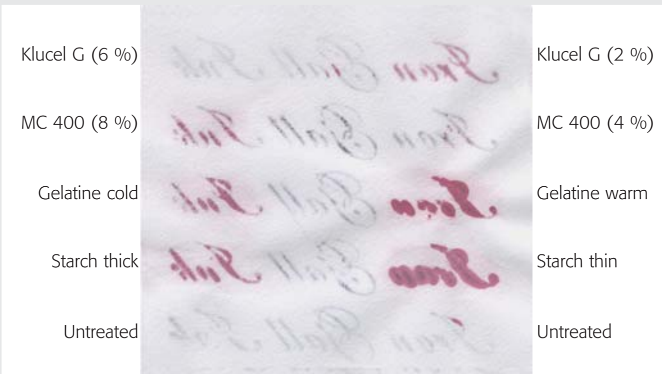
Controlling the Water Content of a Repair

The difficulty to realize a uniform, low quantity of solvent during mending requires a control technique. Therefore, the bathophenanthroline indicator paper was further developed and put on the market for sale (Practice-in-Conservation XXX to complete XXX). The technique is fast, cheap and pragmatic. It enables paper conservators to optimize their own working practice. While in the beginning it is advisable to test the own working procedure at least once a day, after some training the test can be used less often. An experienced conservator who frequently carries out mending of ink corroded objects is recommended to use the test once a week.

Conclusion

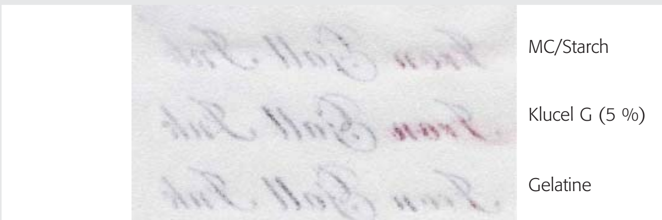
The fundamental outcome of this study is logical but has never been demonstrated - all solvent-based adhesives cause migration of invisible, detrimental components out of the iron gall ink into surrounding paper areas when applied inappropriately. Even Klucel G in Ethanol (96 %), that was always expected to be 'safe' can actually cause iron(II) ions to spread. It appears

13 Iron(II) migration due to brushing adhesive through repair paper (recto).

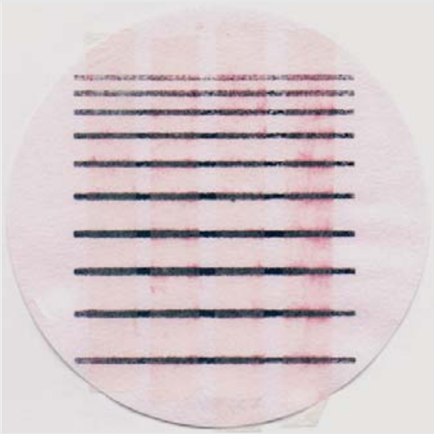


14 Iron(II) migration due to brushing adhesive through repair paper (verso).

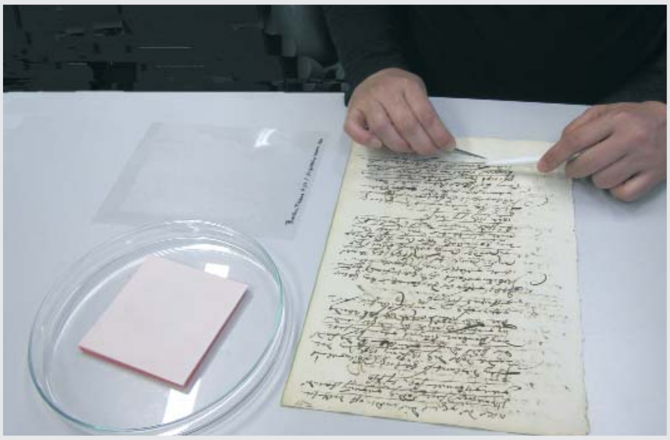
15 Iron(II) migration due to remoistenable tissue (recto). Left: too much water, right satisfying result.



16 Xron(II) migration due to remoistenable tissue (recto). Right: too much water; left: satisfying result,.



17 Iron(II) migration after Repatex application.



18 XXX FOTO Application of a remositenable tissue. XXX

necessary to limit the amount of transferred solvent to such an extent that migration can be limited or even prevented, while achieving a functioning repair on ink corroded areas.

Among all the techniques investigated in this work, the best results were achieved with a self-made remoistenable tissue. This method realizes an adhesive film of even thickness and gives reproducible and satisfying results. Remoistenable tissues allow to minimize the quantity of water to be transferred to the ink area. A specific method to guarantee a similar amount of water for each repair was developed, making use of a kitchen sponge-cloth and two layers of blotting paper on top.

While the Methyl red and the cobalt chloride indicators were not useful, the bathophenanthroline indicator stamped with iron gall ink proved to be an indispensable tool for the conservator to control the amount of solvent transferred during mending. Therefore, it was developed to a ready-to use product and is now available on the market.

Acknowledgements

The research on which this paper is based formed the final thesis of a four year book and paper conservation training at the Netherlands Institute for Cultural Heritage, Amsterdam. We are thankful to all individuals that supported this research, either by replying to the questionnaire, or by supporting this research otherwise. Our special thanks goes to Christina Duran Casablancas (Amsterdam, City Archives), Johan G Neevel (The Netherlands Cultural Heritage Agency), and the paper & photo conservators of the Rijksmuseum Amsterdam.

Endnotes

[1] The period of 25 years is based on our empirical observations on origials.

[2] Solubility of iron(II) sulphate heptahydrate: 25,6 g in 100 ml water (at 20 °C); 48,6 g in 100 ml water (at 50 °C); see <www.chemicalbook.com/ChemicalProductProperty_EN_CB9232125.htm> (visited 29.3.2011) and <www.jtbaker.com/msds/english html/f1802.htm> (visited 29.3.2011).

[3] This part of the experiment was carried out at the Netherlands Institute for Cultural Heritage (ICN, Amsterdam).

[4] Of the 36 paper conservators that answered the questionnaire, 30 conservators do carry out repairs on iron gall ink objects (Jacobi 2009: 55-58).

[5] 'Another. Take a quart of strong wine, put it into a new pot, and set it on a soft fire till it be hote, but let it not seeth, then put into it foure ounces of gauls, two ounces and a halfe of gum Arabike, and two ounces of victriall, al beaten into smal pouder, and sifted through a siue, stirre it with a wooden sticke, and it will be good inke.' The Ink Corrosion Website <www.irongallink.org/make-ink/recipes-and-instructions>, first recipe (visited 14.03.2011).

[6] Dutch tap water is of good quality and is commonly used directly from the tap for conservation purposes.

[7] In reality, a repair would be applied on the reverse side of the ink if possible. However, to estimate the maximum migration in order to minimize this risk, for these experiments, the repair was carried out directly on the ink.

[8] Iron sulphate is commonly considered to be insoluble in ethanol. Actually, this is incorrect, iron (II) sulphate heptahydrate it is slightly soluble in alcohol (Weast and Astle 1979: B87). This solubility might be depending on it's state of hydratisation. Adding iron(II) sulphate heptahydrate to ethanol (absolute, 99,7 %: Aldrich) showed that the salt indeed dissolves. Dipping a bathophenthroline indicator paper into the colourless liquid, positively identified the presence of dissolved iron(II) ions.

[9] Gas chromatography - mass spectrometry analysis (GCMS) showed that those kitchen sponge-cloth consist of pure cellulose,containing a dye that is insoluble in water. English: sponge-cloth; Dutch: sponsdoek; French: Lavettes végétales; German: absorbierendes Abwaschtuch.

References

Brückle, Irene (1996): Update: Remoistenable Lining with Methylcellulose Adhesive Preparation. In: The Book and Paper Group and Annual of the American Institute for Conservation of Historic and Artistic Works, Vol 15, pp 25/26.

Charles, Vanessa (2008): Cold Gelatine Adhesive. In: Papier-Restaurierung, Vol 9, No 3, pp 11/12.

Henry, Walter, et al (1985): 'Mending'. Chapter 25. In: Paper Conservation Catalog. Washington D.C.: American Institute for Conservation Book and Paper Group. Versie 1985. 10 februari 2009 <http://aic.stanford.edu/sg/bpg/pcc/25_mending_PROTOTYPE.pdf>.

Jacobi, Eliza (2009): Lokale reparaties op ijzergallusinkt. Op zoek naar lijm en methode. Unpublished diploma thesis. Amsterdam: Instituut Collectie Nederland.

Kolar, Jana, and Strlič, Matija (2006): Ageing and Stablisation of Paper Containing Iron Gall Ink. In: Kolar, Jana, and Strlič, Matija (eds): Iron Gall Inks—On Manufacture, Characterisation, Degradation and Stabilisation. Ljubljana, National and University Library, Chapter 11, pp 181-194.

Kolar, Jana, et al (2006): Prototype InkCor Treatments: Evaluation of Effectiveness. In: Kolar, Jana, and Strlič, Matija (eds): Iron Gall Inks—On Manufacture, Characterisation, Degradation and Stabilisation. Ljubljana, National and University Library, Chapter 11, pp 181-194.

XXX Literature? Kolbe, Gesa (1999) XXX

Kolbe, Gesa (2001): Gelatine, Eigenschaften und Auswahlkriterien in der Papierrestaurierung. In: PapierRestaurierung, IADA Yearbook 2001 (Supplement). Stuttgart: FotoText Verlag Wolfgang Jaworek, Vol 2, pp 41-56.

Kolbe, Gesa (2004): Gelatine in Historical Paper Production and as Inhibiting Agent for Iron-Gall Ink Corrosion on Paper. In: Restaurator, Vol 25, pp 26-39.

Lichtblau, Dirk, and Anders, Manfred (2006): Designing Non-Aqueous Treatments to Counteract Ink Corrosion. In: Kolar, Jana, and Strlič, Matija (eds): Iron Gall Inks—On Manufacture, Characterisation, Degradation and Stabilisation. Ljubljana, National and University Library, Chapter 12, pp 195-214.

Martin, Aurelie, et al (2011): Local strengthening of mould-damaged manuscripts—A Case study on Logbooks of early French Exhibitions in Louisiana (1684-1722). In: Journal of PaperConservation, Vol 12, No 1, pp 21-29.

XXX Bibliographical title of Neevel 1995? XXX

Neevel, Johan G, and Mensch, Kees (1999): The behaviour of iron and sulphuric acid during iron gall ink corrosion. In: Bridgland, Janet (ed): ICOM Committee for Conservation. Preprints of the 12th Triennial Meeting, Lyon, 29 August-3 September 1999: London: James & James (Science Publishers) Ltd, Vol II, pp 528-533.

Neevel, Johan G, and Reissland, Birgit (2005): Bathophenanthroline Indicator Paper. In: PapierRestaurierrung, Vol 6, No 4, pp 28-35.

XXX Reference? XXX Nguyen, Thi-Phuong, et al (2004): Effects of Gelatine sizing on iron gall ink corroced paper. In: Kolar, Jana, et al (eds): Proceedings of the International Conference: Durability of paper and writing. November 16-19 2004, Lubljana, Slovenia, pp 52/53.

Nguyen, Thi-Phuong (2005): Gelatin as Adhesive. In: PapierRestaurierung. Vol 6, No 4, pp 31-34.

Nijhuis, Sylvia (2006): Gelatine en dierlijke lijm. In: CR: Interdisciplinair blad voor conservering en restauratie, No 4, pp 18-21.

Pataki, Andrea (2009): Remoistenable tissue Preparation and its Practical Aspects. In: Restaurator, No 30, pp 51-69.

Potthast, Antje, et al (2008): Iron Gall Ink-induced corrosion of cellulose: aging, degradation and stabilization. Part 1: Model paper studies. In: Cellulose, Vol 15, No 6, pp 849-859.

Quandt, Abigail (2002): Remoistenable tissue for mending paper damaged by copper pigments. The Walters Art Museum, Baltimore, Handout prepared for the IIC meeting 2002 in Baltimore, USA.

Rouchon, Véronique, et al (2008): Iron Gall Ink Aqueous Treatments—Measurements of Elemental Changes by Proton Induced X-ray Emission. In: PapierRestaurierung, Vol 9, No 2, pp 18-28.

Rouchon, Véronique, et al (2009): The water sensitivity of iron gall ink and its risk assessment. in: Studies in Conservation, Vol 54, pp 236-254.

Rouchon, Véronique (2010) xxx Exact Title pp xxx.

Schellmann, Nanke C (2007): Animal glues: a review of their key properties relevant to conservation. In: Reviews in Conservation. No 8, pp 55-66.

Schweppe, Helmut (1993): Handbuch der Naturfarbstoffe: Vorkommen, Verwendung, Nachweis. Landsberg: Ecomed, p. 469.

Strlič, Matija, et al (2006): Model Studies of the Catalytic Role of Transition Metals. In: Iron Gall Inks—On Manufacture, Characterisation, Degradation and Stabilisation. Ljubljana, National and University Library, Chapter 10, pp 173-180.

Titus, Sonja, et al (2009): Stabilising local areas of loss in iron gall ink copy documents from the savigny estate. In: Restaurator, No 30, pp 16-50.

Ubbink, Kyla, and Partridge, Roberta (2003): Preserving Letterpress Copybooks. In: Journal of the Canadian Association for Conservation, Vol 28, pp 38-45.

van Velzen, Bas (2006): A Morphology of the Tear: a first approach towards a general terminology. In: PapierRestaurierung. Vol 7, No 2, pp 13-16.

van Velzen, Bas, and Jacobi, Eliza (2011): Remoistenable Tissue. In: Journal of PaperConservation, Vol 12, No 1, p 36.

Vuori, Jan, and Tse, Season (2005): A preliminary study of the use of batophenanthroline iron test strips on textiles. In: ICOM Committee for Conservation 14th triennial meeting, the Hague, 12- 16 September 2005. Preprints, Vol II, pp 988-995.

Wagner, Sarah S (1996): Remoistenable Tissue Part II: Variations on a Theme. In: The Book and Paper Group and Annual of the American Institute for Conservation of Historic and Artistic Works, Vol 15, pp 27/28.

Weast, Robert C, and Astle, Melvin (eds, 1979): CRC-Handbook of Chemistry and Physics. 60th edition. Boca Raton: CRC Press.

Wilson, Helen (2007): Analysis of the current research into the chemistry of Iron Gall Ink and its implications for paper Conservation. Honour School of Chemistry: Chemistry part II. St. Anne's College.

Suppliers

'Dutch Fe-Migration Mending Test', Practice in Conservation, claire@practice-in-conservation.com, eliza@practice-in-conservation.com.

Albert Heijn supermarket, Provincialweg, 1506 MA Zaamdam, The Netherlands, www.ah.nl (red wine; demineralised water).

Antonides, Beukenlaan 3, 8536 TK Oosterzee, The Netherlands, Tel +31-882-686643, Fax +31-882-686611, www.antonides.com (Ethanol 96 %, no. I-A5.201.51A).

Conservation by Design, Timecare Works, 5 Singer Way, Woburn Road Industrial Estate, Kempston Bedford MK42 7AW, United Kingdom, Tel +44-123-4846300, Fax +44-123-4852334, www.conservation-by-design.co.uk (Culminal MC 2000, Culminal MC 400).

Fisher Scientific, Postbus 4, 1120 AA Landsmeer, The Netherlands, Tel +31-204-877000, Fax +31-204-877070, www.fishersci.nl (XXX products? XXX).

Gangolf Ulbricht, Werkstatt für Papier, Mariannenplatz 2, 10997 Berlin, Germany, Tel +49-30-6158155, gangolf.ulbricht@p-soft.de (Gossamer tissue 2 g/m^2; Berlin tissue 2 g/m^2; Kozo/Mitsumata fibres).

GMW Gabi Kleindorfer, Aster Str. 9, 84186 Vilsheim, Germany, Tel +49-8706-1094, Fax +49-8706-559, www.gmw-gabiklein dorfer.de (Gelatine, Type B, 'Restoration'; RepaTex® G5).

Kremer Pigmente GmbH & Co. KG, Hauptstr. 41-47, 88317 Aichstetten/Allgäu, Germany, Tel +49-7565-1011, Fax +49-7565-1606, www.kremer-pigmente.de (gum Arabic, no. 63300; gallnuts, no. 37400; iron (II) sulphate heptahydrate, no. 64200; Kluce® G).

Paper Nao, via Conservation by Design (Japanese paper: RK-38 [16 g/m^2; Kozo, handmade]; RK-0 [5 g/m^2, Kozo, machine-made]; RK-00 (3,6 g/m^2; Kozo, machine-made]).

Peter van Ginkel, Dennenlaan 28, 1161 CR Zwanenburg, The Netherlands, Tel +31-20-4074407, Fax +31-20-4074400, www.petervanginkel.nl (wheat starch paste).

De Posthumuswinkel, Sint Luciënsteeg 23-25, 1012 PM Amsterdam, The Netherlands, Tel +31-20-6255812, Fax +31-20-6267149, www.posthumuswinkel.nl (rubber stamps).

Sigma-Aldrich Chemie B.V., Postbus 27, 3330 AA Zwijndrecht, The Netherlands, Tel +31-800-0229088, Fax +31-800-0229089, www.sigmaaldrich.com (Bathophenanthroline [no. 133159 - 500 g]; Methyl Red [no. 250198 - 25 g]; Cobalt (II) chloride hexahydrate [no. 255599 - 5 g]); ethanol anhydrous [no. 459836 - 100 ml].

Whatman Inc, 200 Park Avenue, Suite 210, Florham Park, NJ 07932, USA, Tel +1-973-245-8300, Fax +1-973-245-8324, www.whatman.com (filter paper, no. 1441 090, Ø 9 cm).

Authors

Eliza Jacobi holds an MA in Modern Art History, with a minor in museum studies, of the University of Amsterdam. After her graduation in 2004 she worked during three months in the library of the Dutch University Institute for Art History in Florence. In 2009 she completed a four year long book and paper conservation training at the The Netherlands Institute for Cultural Heritage. As a part of these studies, she completed two five month internships, first at Lingbeek Papierrestauratie in Haarlem, The Netherlands (2008) and then at the Book and Paper Conservation Studio in Dundee (Scotland, 2008). In 2009 she worked voluntary in Yogyakarta, Indonesia, directing a conservation and digitization project in the library of the Kraton (the Sultan's palace) during a period of four months. Since February 2010 she has been working as a paper conservator in the private conservation studio 'Mooie boeken en papierwerken' in Amsterdam.

Eliza Jacobi, Laurierstraat 97b, 1016 PK Amsterdam, The Netherlands, Tel +31-6-10271387, elizajacobi@gmail.com

Birgit Reissland completed the Paper Conservation Program at the 'State Academy of Art and Design' Stuttgart in1997. Since then she has been working at the conservation research department of the Netherlands Institute for Cultural Heritage in Amsterdam, which has become part of the Dutch Cultural Heritage Agency since January 2011. She is guest lecturer at the University of Amsterdam, editor in chief of the 'Journal of Paper-Conservation' and 'The Iron Gall Ink Website'.

Birgit Reissland, The Netherlands Cultural Heritage Agency (RCE), Movable Heritage Knowledge Sector, Ateliergebouw, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands, Tel +31-20-3054-702, b.reissland@cultureelerfgoed.nl

Bas van Velzen became involved in paper-conservation via his interest for the printing profession. Between 1980-1984 he received his training as a conservator in Amsterdam. Together with running his own studio he teached paper conservation since 1995. From 1998 he combined working as a conservator for ICN (Netherlands Institute for Cultural Heritage) with teaching at the ICN conservation education programme. He is the senior tutor book- and paper conservation at the University of Amsterdam conservation and restoration programme since 2007

Bas van Velzen, Senior tutor book- and paper conservation, University of Amsterdam (UvA), het Ateliergebouw, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands, Tel +31-20-6747-488, bas.van.velzen@uva.nl

Claire Phan Tan Luu holds a Msc in chemistry of the university of Aix-Marseille III. In 2009 she graduated form the University of Sorbonne-Paris I in book and paper conservation. As a part of this study she did an internship for one year at The Netherlands Institute for Cultural Heritage under the supervision of Birgit Reissland and Frank Ligterink on the ink corrosion prognosis tool. Since 2010 she is involved in the project " side effects related to values" within the Metamorfoze gouvernemental program from the Netherlands.

Claire Phan Tan Luu, Afrikanerplein 15/2, 1091 PN Amsterdam, The Netherlands, Tel +31-6-4465 9303, claire.phantanluu@gmail.com

Frank J. Ligterink studied books and documents conservation at the Opleiding Restauratoren (Netherlands Programme for Conservation Training) in Amsterdam between 1985 and 1989. His thesis was directed to the study of foxing stains in books. He subsequently obtained a Masters degree in theoretical physics from the Vrije Universiteit in Amsterdam, including an additional title as a school teacher of physics. He has been working since 1996 as a research scientist at the Instituut Collectie Nederland (Netherlands Institute for Cultural Heritage), which has become part of the Dutch Cultural Heritage Agency (Rijksdienst voor het Cultureel Erfgoed) since January 2011, both in the research department and as science teacher in the conservation training program. His research interests include a range of interdisciplinary topics and projects designed to bring together the worlds of physics and conservation. Some of the most prominent include: foxing and discoloration of paper, cellulose acetate decay and stabilisation, microclimatic studies, colour and colour change, risk management, and models for prioritising research strategies in conservation.

Frank Ligterink, The Netherlands Cultural Heritage Agency (RCE), Movable Heritage Knowledge Sector, Ateliergebouw, Hobbemastraat 22, 1071 ZC Amsterdam, The Netherlands, Tel +31-20-3054-702, b.reissland@cultureelerfgoed.nl