INGRID SCHWARZ

Academy of Art and Design, Stuttgart: The Book and Paper Conservation Program and Current Research
2. A Pre-packaged α-Amylase Poulticing System: Albertina-Kompresse

ABSTRACT

Starch paste, when used as a mounting adhesive modified with additives such as protein glue or alum, frequently causes damage to paper as a result of its embrittlement. Starch digesting enzymes, e.g. α –amylase, in immersion or as a gel poultice are applied to facilitate its removal. Disadvantages of a gel poultice is its complicated preparation, especially in case of minimal enzyme concentration and its limited stability to biological infestation.

This project aimed at developing a method that is easy to use and well controlled for employing enzymes locally without the need of a subsequent wet treatment. The focus of this research was to choose and examine different materials to assure a precise and non-damaging application of enzyme poultices. A previously patented amylase-gel recipe has been used to imbue a special material. An appropriate synthetic, inert non-woven fabric serves as the poultice carrier. An interleaf paper prevents the transfer of the gel-forming agent onto the paper but allows the enzymes and sufficient humidity to pass to the area to be treated. The poultice assembly is completed by an absorbent non-woven fabric to guarantee homogeneous humidification during the treatment time. Directions for the application and use of this poultice were carried out through experiments on mock-ups. The product developed can now be stored in its dry state and activated by adding a minimal amount of water. The amount of enzyme residues are so insignificant that no rinsing after treatment is required. Successful application of the so-called "Albertina-Kompresse" is demonstrated on a number of items from the Vienna Albertina Graphic Collection, the Kupferstichkabinett of the Hamburg Kunsthalle, Germany, and other collections.

This project was conducted as a senior thesis at the Book and Paper Conservation Program at the Academy of Art and Design, Stuttgart. Presented at the Book & Paper Group Session, AIC 28th Annual Meeting, June 8–13, 2000, Philadelphia, Pennsylvania. Received for publication Fall 2000.

INTRODUCTION

It has long been common knowledge for conservators that starch paste can be liquefied by enzymes known as amylases (Wendelbo and Fosse 1970). To apply these biocatalytic agents and to produce enzyme solutions or gels under the regular working conditions of a conservation studio still proves complicated. General recommendations for the application of enzymes have been published in the past. Unfortunately, so far there have not yet been found reliable, reproducible techniques for the application of enzymes which can be regarded as standard methods in paper conservation (Segal 1994; Grattan 1980; Erickson 1992; Tse and Burgess 1994).

The goal of the research in the present project was to develop a prefabricated amylase poultice. It facilitates the simple and local enzymatic removal of non-swellable starch-based adhesives that contain admixtures like alum and/or protein glue from paper and requires only a minimal amount of moisture. The pre-packaged α –amylase poulticing system—which is available under the name "Albertina-Kompresse"—is the result of extensive cooperation between conservators and scientists, universities and industrial research laboratories.

This enzyme poultice was originally developed for the treatment of a special problem in the conservation of nineteenth-century prints which occurred in the Albertina in Vienna (Blüher et al. 1999). In the Albertina more than one hundred thousand items in their collection of nineteenth-century prints are stored in albums. The prints are mounted onto the blank, bound book pages. Prints like the one shown in figures 1 and 2 were adhered at the corners and edges with adhesive points. Usually six adhesion points can be found.

Pure wheat starch paste was commonly used in the past for mounting graphic artwork. It can be considered a suitable mounting adhesive because of its well known adhesive power and its permanent elasticity within humidity changes (Stadlinger 1932, 6). In addition, it remains

Fig. 1. In the case of the Albertina albums the prints were mounted on the blank pages with adhesion points. The mounting with modified paste results in tension, formation of folds, dents, and creases as can be seen in the corners of these prints.

Fig. 2. Distortion of an intaglio print tensioned by mounting strips attached along all four edges. Arthur Illies, Three tulip blossoms, 1927, color zinc etching on Japanese paper.

easily removable by swelling with moisture, even after centuries.

In the case of the Albertina albums the paste was modified with additives such as alum and protein glue, which causes damage as can be seen in figures 1 and 2. These substances were added to improve the adhesive power and to reduce the pastes' sensitivity towards microbiological infestation (Lehner 1932, 60). Nowadays it turns out that the modified paste becomes inflexible and hydrophobic. Since this paste does not react as strongly to changes in humidity as a pure starch paste, we find severe cockling and corner draws on the works of graphic art in the Albertina albums.

A similar problem is presented by a mounting technique used in graphic collections at the beginning of the twentieth century. Figure 2 shows a print from the collection of the Hamburg Kunsthalle. Prints on Japanese paper are attached onto a mat with Chinese paper strips along all four edges, a technique suggested by H. Singer in 1916.[1] Again serious distortion has been caused most probably by fluctuations of humidity, because the paper was unable to expand evenly. The phenomenon of cockling paper can have such great impact that it results in abrasion of the printing ink.

The objective of our research was to find a way of dismounting these engravings and lithographs to protect them from further destruction, for example, or for exhibition purposes. At the same time ensuring no damage—such as tidelines or fiber losses—should be caused to either the print or its mount.

Traditional techniques of humidification, e.g. the application of Gore-Tex humidifying poultices or aerosols or warm water steam, failed to soften the adhesive joint to a sufficient extent (Banik 1991). Especially with soft papers the high viscosity of the swollen paste does not permit a loss-free separation of the originals from mechanically more stable carrier papers.

Even archival material which has been mounted or coated with starch paste frequently cannot be separated by traditional humidification methods. This is especially the case when water-sensitive color media are present in the area under treatment or when there are fragile areas in the paper caused by iron gall ink corrosion (Burgess and Charette 1981). For this reason it is of great significance, on

the one hand, to reduce the amount of humidity needed for separation; on the other hand, the greatest possible solubility of the starch paste needs to be obtained.

STARCH REMOVAL USING ENZYMES

The use of enzymes is highly effective when the paste cannot be removed by moistening and swelling with water. Enzymes are proteins that act as bio catalysts having distinct specification for certain substrates. As catalysts they accelerate specific chemical reactions in aqueous solution or at least in the presence of sufficient moisture at moderate temperatures and pH conditions. Presence of water is of decisive importance for making the catalytic action of enzymes possible.[2] Amylase is a starch digesting enzyme that liquefies hardened starch paste areas (Robyt 1984; Lehninger 1987, 229).

The main component in the mounting adhesive is starch, a polysaccharide photosynthesized by green plants. The macromolecules are built up by α –D-glucopyranose. In contrast to cellulose, which is built up by β–1,4 glucosidic bonds, the units building up starch are exclusively linked together by α–1,4 glucosidic bonds. α–amylases catalyze the hydrolysis, i.e. the splitting, of only α–1,4 glucosidic bonds in polysaccharides randomly across the molecular chain. As the reaction is specific, decomposition of cellulose cannot be catalyzed by amylases (Grattan 1980, 16–17). The enzymatic decomposition of starch is shown schematically in figure 3.

An indication for starch is iodine, which stains starch intensely blue (Holló 1968). We applied this indicator to test the ability of the enzyme poultice. This is explained in detail in the experimental part of this publication.

METHOD

A balanced assessment of the risks and chances of the proposed enzymatic removal of modified starch paste requires a thorough study of a method that can be easily controlled and used to employ the enzymes locally. The main intentions for the separation of the prints stored in the Albertina albums was to avoid damaging both the prints and the albums. An important requirement was that no subsequent wet treatment should be necessary, firstly because of the number of prints to be detached and secondly to avoid disbinding the albums. This means the procedure must reliably exclude tideline formation or deposition of residues on the treated items.

The first step of the entire procedure was the development of an enzyme gel based on a cellulose ether. Concentration of enzymes and additives were reduced to an absolute minimum, which made it possible that only insignificant residues remain in the papers. The gel functions perfectly to solubilize the modified starch paste

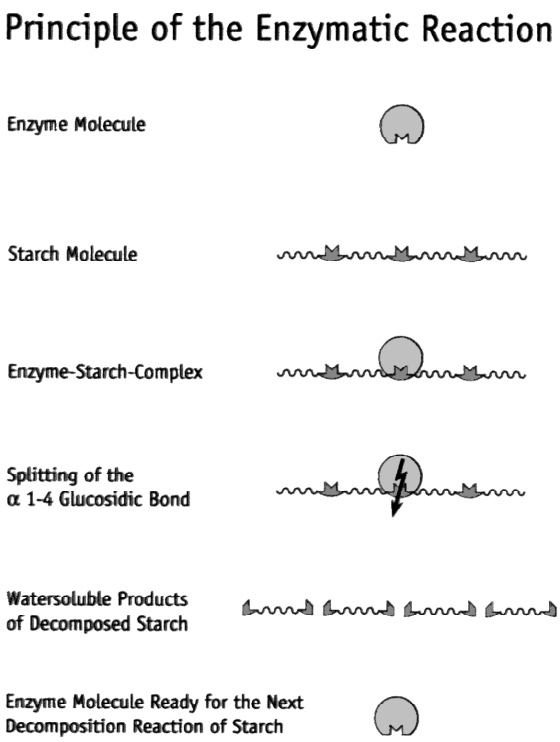

Fig. 3. Enzymatic decomposition of starch

(Hatton 1977; Chapman 1986; Blüher et al. 1996; Lidle-Fürst 1999).

We applied this gel locally on the paper within the pasted area, allowing the enzymes to migrate with the moisture vertically through the paper to the starch paste. In order to achieve an even decomposition of the paste it is necessary to guarantee undisturbed and homogenous migration of enzymes. That means the gel requires a moderate weight, especially when the paper surface is uneven. Laying a weight on a drop of enzyme gel is not a recommendable solution. This would lead to difficulties, since the gel might squeeze out far beyond the area where the two papers to be separated are mounted together. As mentioned above, two additional factors made the use of amylase gels complex: its complicated preparation, which needs special equipment, and its limited stability towards biological infestation.[3]

Accordingly, in the second stage of the project we developed a method of delivering the enzymes in a stable form with the possibility of applying moderate weight. Our solution is to use a synthetic, inert non-woven fabric that is soaked with the enzyme gel and then dried. In this dry state the enzymes are in a stable form. The special fabric accumulates just enough enzyme gel to be effective and the poultice can be used whenever it is necessary. With the addition of water the methyl cellulose swells again and the enzymes are ready to react with the starch (Schwartz et al. 1999). Hence the application technique and possibilities

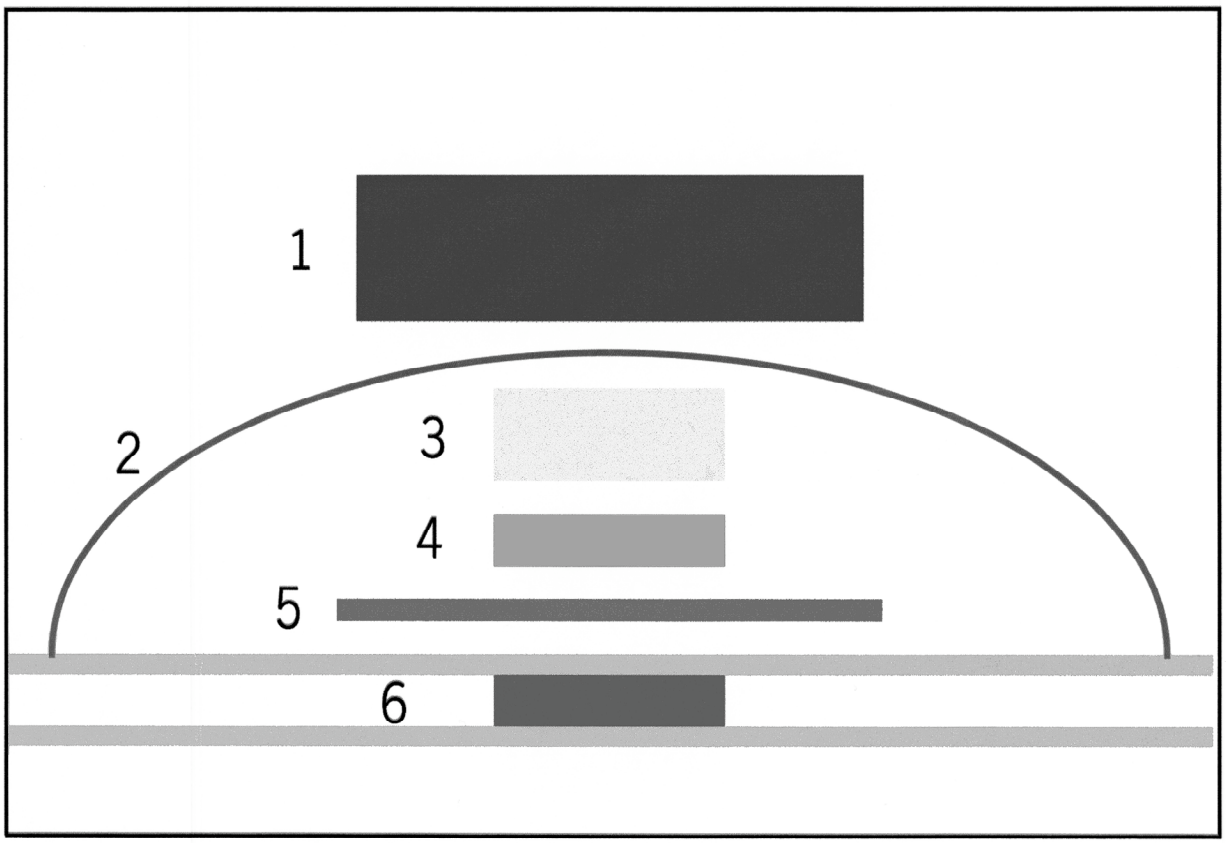

Fig. 4. Application structure of the enzyme poultice. 1, weight; 2, polyester film; 3, moistening material; 4, enzyme impregnated poultice; 5, interleaving paper; 6, papers with starch paste in between. From *Albertina Kompresse*, folder and application directions, Klug Conservation, Immenstadt (2000).

of its use are described and assessed in this paper as well as an experimental part about the materials used and aging effects are given.

APPLICATION

Two papers mounted together are often more or less wavy. The amylase poultice generally is to be applied locally in the area of the adhesive joint in order to avoid contamination of the treated item as much as possible. The poultice consists of three layers:

- a synthetic non-woven fabric impregnated with the amylase gel;
- an interleaf paper;
- a water retaining material.

The complete structure is schematically shown in figure 4. Figures 5–8 present the application of the enzyme poultice in detail. A Chinese paper strip is pasted onto the verso of one of the prints on Japanese paper, part of the collection of the Hamburg Kunsthalle.

The item under treatment is placed on a polyester film (Mylar) which serves as a base work surface. All materials are cut to the shape specifically needed. Firstly the moistened interleaf paper is placed onto the hinge paper. The function of the interleaf paper is to prevent any transfer of the gel-forming cellulose ether and at the same time allowing the migration of the enzyme and auxiliary components to the adhesive joint. After that the non-woven fabric containing the enzyme is placed onto the interleaf paper, likewise evenly moistened with a brush (fig. 5). The amount of water needed is about 0.08 ml/4 cm^2 of the amylase poultice. The poultice composition is completed using an absorbent fabric for even humidification (fig. 6). Finally, the poultice is covered with a piece of Mylar and a moderate weight (fig. 7). In the presence of sufficient humidity the enzymes migrate through the paper to the adhesive layer. Through the enzymatic action the starch paste is decomposed and consequently solubilized—losing its adhesive power completely. As in this example, the paper strips could be taken off after twenty minutes (fig. 8).

When it comes to thicker papers, with this amount of water the reaction time will be longer. The total treatment time for detachment of starch paste mounts goes up to ninety minutes. The time depends mainly on the structure of the treated papers and the amount of water used. Relevant for the first factor is the thickness of the paper

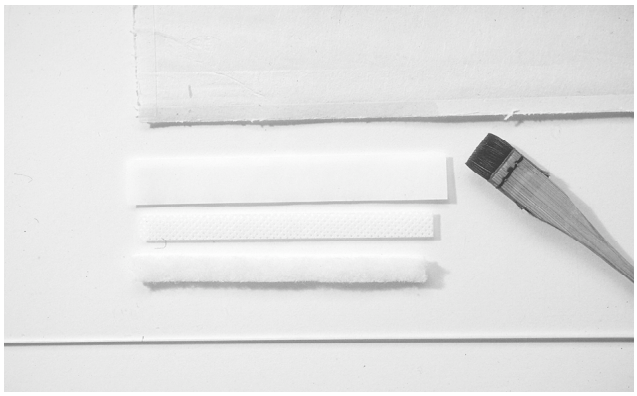

Fig. 5. Above: paper interleaf; center: enzyme impregnated poultice; below: moistening material

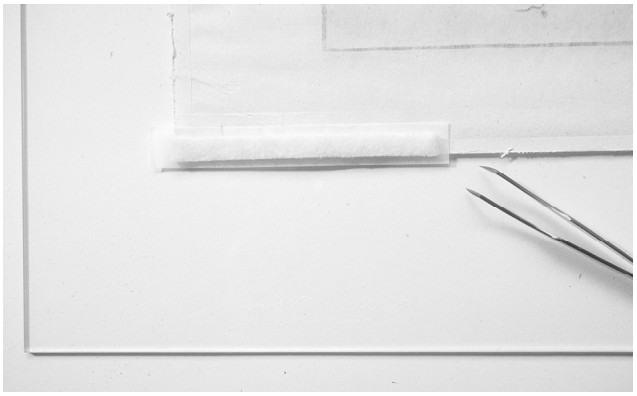

Fig. 6. Applying the poultice material

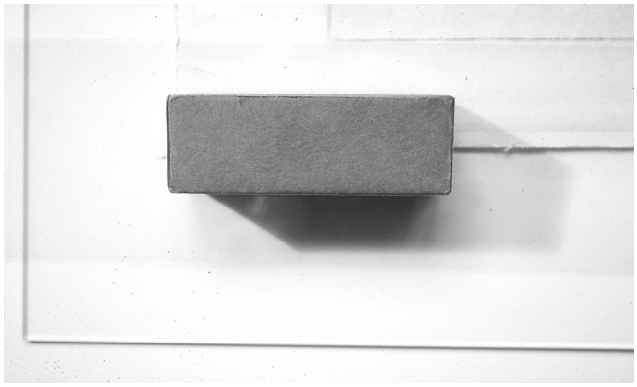

Fig. 7. Treatment of the amylase poultice under moderate weight

Fig. 8. Detachment of the paper strip and removal of adhesive residues

and its amount of sizing, which counteracts the migration of humidity and enzymes. The second factor is the amount of water used for the application of the enzyme poultice, which can be tailored to the need of the individual object. For objects that are extremely sensitive to water, the moisture must be minimized in order not to affect the media. This is the case with such very soft Japanese paper or very water-sensitive color media.

In the case of detachment of fully relined works of art, e. g. Japanese woodcuts which have often been relined with starch paste adhesives, the problem of water-sensitive color media can be highly significant. The sensitivity of the color media makes the application of traditional humidification techniques for detachment impossible. Partial humidification with cotton swabs followed by the mechanical removal of the support paper is a time-consuming technique. It leads to wet-dry interfaces and includes expanding and partial warping of the Japanese paper (Dupont 1996). The advantage of applying amylase poultices on large areas for Japanese woodcuts is the minimal amount of moisture needed. The poultice just allows the enzymes to work but leaves the sensitive color media stable and prevents wet-dry interfaces and deformation of the paper (fig. 9) (Schneller 2000).

EXPERIMENTAL DESIGN AND RESULTS

All components and materials needed to set up an enzyme poultice were tested intensively.[4] The first objective was to choose the most suitable non-woven fabric from different options for poultice materials, interleaving

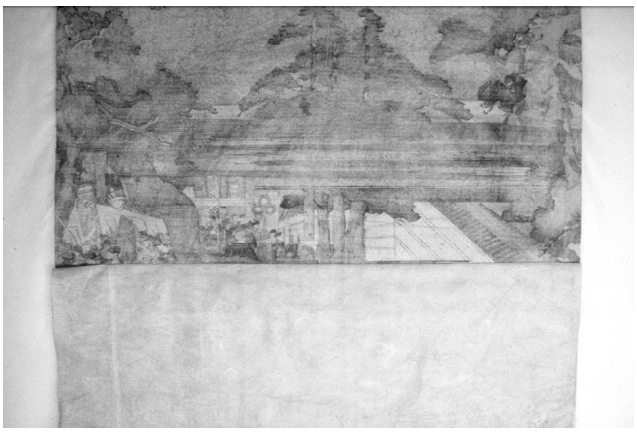

Fig. 9. Japanese woodcut (above) being detached from its support (below) after a thirty minute application of a large-area amylase poultice. Kuniyoshi, Utagawa, Inv.-Nr. N. E. 7278, Albertina, Vienna.

papers, and moistening materials. The research included the development of a mechanized process to impregnate the poultice non-woven fabric with the enzyme gel. After determination of the most suitable materials, directions for the application and use of this poultice were developed.

In order to choose the materials it was necessary to evaluate the effectiveness of the transfer of enzymes and auxiliary components from the carrier material to the starch paste adhesive joint. Samples of materials were examined through experiments using the starch-iodine color reaction on mock-ups. Long term effects of the application of the enzyme poultice under different conditions were studied by means of artificial and natural aging.

Enzymatic activity can be evaluated with the starch-iodine color-reaction (Blüher et. al. 1996, 497). For this test a filter paper is soaked in a 0.2% solution of cold-water-soluble starch and then dried. Before the application the filter paper is dipped in a 0.01% aqueous solution of iodine-potassium iodine, thus causing an intensive blue staining. The action of the amylase poultice on the colored sample results in fading and loss of the blue-violet color according to the molecular decomposition of the starch. By this test the optimal non-woven fabrics and interleaf papers could be evaluated. An example of the results is shown in figure 10.

The synthetic non-woven fabric chosen is mechanically strong. On one hand this mechanical stability is an important factor for the impregnation process, on the other for the application. It is flexible enough to adapt to uneven surfaces. The fabric accumulates just enough enzyme gel to be effective.

Both the interleaf paper and the moistening material were likewise tested with the starch-iodine reaction on mock-ups. The cellulose tissue interleaving paper guarantees the diffusion of humidity and enzymes to the starch paste. It does not allow the gel thickening agent to deposit on the paper. To keep the enzyme poultice evenly humid for a period of up to ninety minutes, a highly flexible synthetic non-woven fabric or blotting cardboard can be applied.

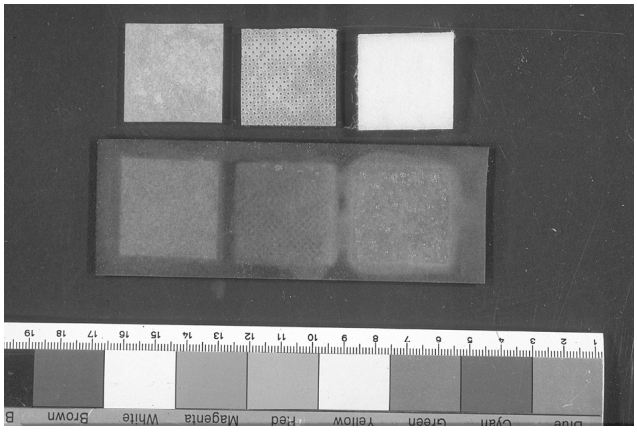

Fig. 10. Enzymatic action (twenty-minute) using different poultice materials compared by means of the starch-iodine color-reaction. The sample on the left shows the most even and efficient enzymatic decomposition of starch.

Experiments done on mock-ups were performed to develop the application technique for the poultice system which has been described above. Mock-ups were then examined to observe the deposition of residues on the treated items. Of decisive importance for the safe applicability of the poultices was to keep the residual amount of enzyme and auxiliary additives within the paper on the lowest possible level. It clearly proved that the amount of amylase residues within the paper was very low, ranging from 2.3 μg to 7.6 μg related to 3 cm^2 of a copperplate board (150 g/m^2). These already small concentrations of enzyme residues within the paper can be further reduced to zero if the poultice is applied on the mounting or carrier paper to be detached because the enzyme will not migrate into the item during the necessary treatment time for the detachment.

As to the auxiliary components, a small amount of residual wetting agent remains in the paper after treatment which ranges from 46.7 to 6.8 μg.

Further it proved that the degree of polymerization of the cellulose remains unchanged after treatment because the amylase used for poultice preparation is free of products that would affect or decompose the cellulose.

Long term effects on the application of the enzyme poultice were studied intensively after different conditions of application by means of artificial aging, i.e.: thermal (in accordance with ISO 9706); dynamic (90°C with fluctuating relative humidity, 80%, 35%, 3-hour cycle); and light aging (Xenotest). No discoloration related to residues was found on treated papers as a result of aging. This supports the analytical data from the enzyme residue analysis, as higher amounts of residues would have caused a yellow to brown discoloration.

CONCLUSION

The pre-packaged α–amylase poulticing system for the simple and local removal of starch based mounting adhesives and additionally for removal of complete relinings within one working process has been developed and tested on mock-ups as well as in routine conservation practice. It could be demonstrated that this amylase poultice can be used as a reliable standard technique for detachment of mounted prints and drawings. The poulticing system includes a special non-woven fabric which is soaked with an amylase gel and dried. The amylase poultice can be stored at least twelve months under dry and cool conditions and easily activated by moistening.

Practical application demonstrated clearly that the poultice allows for safe separation of particularly sensitive and damaged papers. Even in presence of sensitive media, the application technique can be handled systematically with a minimum amount of moisture without loss of fibers. The technique not only allows the conservator to work locally on starch-based adhesive joints but even to detach fully relined works of graphic art from their support. The prefabricated amylase poultice has been very successfully applied to a number of prints and drawings in several European collections such as the Albertina, Vienna, Hamburg Kunsthalle, Weimarer Klassik Foundation, and other archives in Germany.

ACKNOWLEDGMENTS

The project to develop the pre-packaged α–amylase poulticing system has been supervised and supported by scientists, companies, foundations, and graphic art collections. The author wishes to express her thanks to Prof. Dr. Gerhard Banik, Dr. Agnes Blüher, and Barbara Hassel, Academy of Art and Design, Stuttgart, for supervising the project and the scientific support.

The technical and financial support from Henkel Central Eastern Europe, Vienna; Henkel KGaA, Düsseldorf; Klug Conservation, Immenstadt; and the Forschungsförderunsfonds für die Gewerbliche Wirtschaft, Vienna, is gratefully acknowledged.

Special thanks for executing residue analysis to K. H. Maurer and Schmitt (Henkel KGaA, Düsseldorf). The author would also like to thank the following for valuable suggestions and support: Gerlinde Römer (Hamburg Kunsthalle), Hannah Singer (Albertina, Vienna), Monika Lidle-Fürst (Weimarer Klassik Foundation, Weimar) and Christa Hädrich (Staatliche Kunstsammlungen, Kupferstichkabinett, Dresden).

NOTES

1. "All the elder and at least the valuable in case of the newer prints, especially those on thin and light paper must be glued on all four sides. A wheat starch paste is used to which a little alum is added . . . ." Transcription of: "Alle älteren, von den neueren wenigstens die wertvollen Blätter, besonders solche auf dünnem, leicht fliederndem Papier, müssen auf allen vier Seiten aufgeklebt werden. Man benutzt dazu einen Weizenstärkekleister, dem ein wenig Alaun beigesetzt worden ist . . . ." (Singer 1960, 63).

2. More information about the main function of water in enzymatic action in: Gupta 1992.

3. After about two weeks the gel becomes milky. The amylase activity on starch paste decreases noticeably.

4. Experiments, results, and application are described in detail in: Schwarz et al. 1999, 232–237.

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INGRID SCHWARZ
Stiftung Saarländischer Kulturbesitz
Saarland Museum
Saarbrücken
Germany
restaurierung@saarlandmuseum.de