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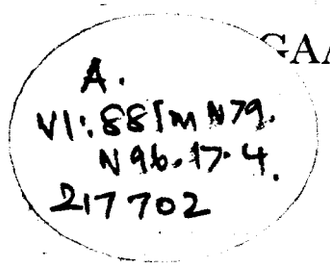

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Ascertainment of the Original Technology for Manufacturing Leather Used for Gospel-Book Binding

by DIANA P. NIKOLOVA & MARIA P. VELCHEVA

INTRODUCTION

A gospel-book, presumably from the end of the 19th century, was stolen and then thrown into a river where it lay for several days. Only two leaves from the book block survived but it was possible to preserve the richly decorated binding (Fig. 1). The binding is of dark blue leather with blind impressions representing the Four Evangelists and some ornamentation. In the middle of the front cover there is a silver medallion, representing an angel praying to Jesus Christ; in the four corners there are small protecting plates; and at the front edge there are clasps. The conservation problem was to find an appropriate finish for the blue leather. The most suitable finish would have been something based on the original components, binding media as well as colour. Therefore it was necessary to ascertain the original technology in the manufacturing of the leather.

PREPARATION OF SAMPLES AND ANALYTICAL TOOLS

It was necessary to find leather samples for analysis, even if only very small ones, and particularly from areas least affected by the damage. These samples were taken from under the silver applications and from the back of the covers, i.e. the small bands under the fly-leaves.

First the elemental composition of the leather was analysed. This was done by qualitative emission spectral analysis (Carl Zeiss Jena apparatus, Germany).

Then the shrinkage temperature of the leather was measured according to the Bulgarian Standard BDS-9057-71.

Finally the leather was examined for vegetable tannins using the $FeCl_3$ test.[1]

In order to isolate the blue dye from the coating, a leather sample was treated twice with a fresh 0.5% solution of lipase enzyme (Milles Lab. Inc., Elkhart,

Indiana, USA) in a 0.1 M phosphate buffer (pH 7.2) for three hours at 30°C. The buffer contained 0.01% Triton X-100 (Sigma Chemie GmbH, Germany). The extract (extract A) was concentrated in vacuo, and then part of it was examined by thin-layer chromatography (TLC) for lipid content. The enzyme-treated leather sample was again extracted, this time with methyl alcohol at 35–40°C with a drop of glacial acetic acid (extract B). The two extracts A and B were collected and concentrated to dryness (sample 1). The dye was re-extracted with distilled water, filtered through "blue label" filter and evaporated to dryness (sample 2).

For purifying the dye, analytical and preparative TLC was performed on silica gel plates 60 F_{254} (Merck, Germany). A solvent system of butanol : glacial acetic acid : distilled water (50:10:20)[2] was used. The densitograms were measured in a reflection mode at wave length 620 nm on a Shimadzu CS-930 densitometer (Japan) using zigzag scanning. The dye was finally purified by gel chromatography on a Sephadex LH-20 (Pharmacia Fine Chemicals, Uppsala, Sweden) on a column (300 mm×10 mm I.D.) eluted with methyl alcohol at a flow rate of 0.1 ml/3 min.

Analysis

The dye was identified as methylene blue by TLC, quantitative reaction and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Methylene blue as double salt with zinc chloride (Merck, Germany) was used as a reference substance in TLC using the developing system described above. Quantitative reaction with ascorbinic acid was applied.[3] ^{1}H-NMR spectra were recorded at 250 MHz on a Bruker WM-250 (Switzerland) in deuterium water (D_2O).

Aluminium (Al) and silicon (Si), most probably from the river soil, were found by quantitative microchemical reactions after the treatment of the sample with 3n HNO_3, Al with morin and Si with ammonia molibdate and benzidine.[4]

A pink impurity in sample 1 was identified as a derivate of methylene blue in the following way. A saturated solution of $K_2Cr_2O_7$ in 5% HCl was dripped onto a piece of a filter paper, as was a methylene blue solution in 5% HCl close by. A pink-coloured band appeared on the border between the two spots.

In order to find oil-binding media in the leather coating, the TLC separation of extract A was performed in a solvent system of hexane : ethyl ether : acetic acid (70:30:2). The chromatogram was detected by a 50% bichrome mixture.[5] Polymerized linoleic and linolenic acids and linseed oil at high temperature were used as reference substances. The linseed oil was treated with lipase after the polymerization.

Results and Discussion

The Leather

The structure of the leather was compact. It had been machine-split. The shrinkage temperature was 118°C which is typical for chrome-tanned leather.[6,7] The test with $FeCl_3$ for vegetable tannins was negative. One of the main components in the leather was found to be chromium (Cr) according to the emission spectral analysis. These data showed that the leather was tanned with chrome salts. The emission spectral analysis showed that aluminium, silicon and titanium were the other main components of the leather sample. Lead (Pb), iron (Fe), calcium (Ca), zinc (Zn) and silver (Ag) were registrated as micro components. The microchemical qualitative reactions showed that the aluminium and silicon determined by emission spectral analysis originated from river soil deposited in the leather pores. These results excluded the possibility of chromium-aluminium or chromium-silicon combination tanning. The chromium-titanium tanning could also be excluded because patents for the actual production of this tanning method were published only in the period from 1969 to 1976.[8,9] Tanning with silicon and titanium salts has been investigated and applied in Bulgaria,[10] but the kind of leather binding used for the gospel-book was made in Bulgaria only up to the end of the Second World War. The conclusion drawn from the experimental data was that the analysed leather was tanned only with chrome salts.

The presence of titanium as a main element in the leather sample could be explained by assuming the presence of TiO_2 as a component of the colour coating of the leather. The manufacture of TiO_2 began around 1920 in Norway and USA[11] and later in Germany.[12] It has been applied as a pigment in different industrial branches including the leather industry. New developments in the leather industry came quite quickly to Bulgaria at that time. The machinery and auxiliary materials for this industry, such as dyes, lubricants, tannins and pigments, were imported after the First World War, primarily from Germany but also from Switzerland and USA.[13] The old Bulgarian leather factories prepared their own formulas, using Russian literature in which TiO_2 was very popular as a component for leather coatings.[14] It is clear that TiO_2 was known in the country only after 1920–1925.

Medallions such as that on the front cover are also to be found on several other gospel-books dated 1920–1930.[15] This kind of gospel-book binding was made in Bulgaria up to the end of the Second World War. On the basis of these facts it was concluded that the leather binding could be dated to the years 1925–1945.

Coatings with binding media of proteins, nitrocellulose and linseed oil were widely used during this period[13,14,16] as was a combination of nitrocellulose and

linseed oil.[17,18] Linseed oil lacquers were generally applied over nitrocellulose ground coats. It is known that the nitrocellulose coatings have a bronze nuance and they are polished with difficulty. These unwanted effects were overcome by treating the coatings with linseed oil before polishing.

The Coating

The first attempt to isolate the colour component (which unavoidably destroyed the leather coating of the sample) was with a solution of Trypsin (Novo Nordisk, Bagsværd, Denmark). The attempt was unsuccessful. It could therefore be concluded that the binding media were not proteinaceous.

The destruction of the sample coating with the lipase solution suggested the presence of oil-binding media. Many organic dyes are non-specifically reversible inhibitors of enzymes.[19,20] That is why a high concentration of the lipase solution was applied for a satisfactory effect from the enzyme action.

Fats and oils have also been used to lubricate leathers. It was clear that both the binding media of the coating and the lubricant in the leather sample were destroyed by the lipase. It is known that neatsfoot oil and cod oil treated with sulphuric acid were used for fat-liquoring chrome-tanned leather in Bulgaria during the period at which the object was dated.[13] These oils do not contain linoleic and linolenic acids,[21] which are the main components of linseed oil. Both fatty acids were found in extract A during the TLC examination, which supported the conclusion that the binding media of the upper layer of the coating were of linseed oil.

In accordance with this result, the presence of lead and iron in the leather tested by the emission spectral analysis was an indication of the possible use of siccatives in preparing the lacquer. These could have been white lead ($2\text{-}PbCO_3 \cdot Pb(OH)_2$), massicot (PbO), lead sugar ($Pb(CH_3COO)_2 \cdot 3\ H_2O$), or Berlin blue ($Fe_4[Fe(CN)_6]_3$[13,17]).

The treatment with lipase was effective for extracting a small part of the dye included in the surface coating (sample 1). The other dye could only be extracted after treating the coating with glacial acetic acid (sample 2). This acid is the very best solvent for nitrocellulose.[22] A shroud of a jelly-like transparent substance remained on the inner surface of the flask after the evaporation of the dissolving agent. This substance became milk-white during the water extraction of the dye. Such an effect is typical of nitrocellulose solutions.[14] These results indicated that the binding media of the lower layer of the coating might be nitrocellulose.

The Dye

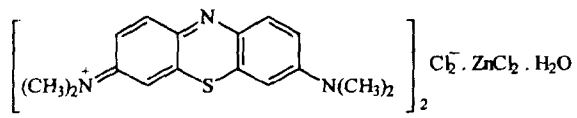
Methylene blue as a double salt with zinc chloride was used in the first half of this century in the leather industry[23,24] as well as in other manufacturing. The

Fig. 1. The leather binding of the gospel-book: a general view before conservation.

drop reaction between the dyes from samples 1 and 2 was positive for methylene blue. The reaction, however, is not strongly specific for this dye. It can only limit the perimeter of blue dyes which are reduced by ascorbic acid to their leucoforms.

The presence of zinc in the blue dye from samples 1 and 2 was proved by micro-chemical reaction with ditizone.[4] A chloroform extract of the dye was used in order to avoid the influence of possible zinc impurities in the leather. Methylene blue as a double salt with zinc chloride was used as a reference substance for TLC in the above experiment.

The blue dye from both colour layers of the leather coating (samples 1 and 2) was same: methylene blue, the main phenothiazine dye:



The TLC separation of sample 2 is shown in Figs 2 and 3. The presence of two blue spots in the chromatogram of the reference substance and of three spots in the chromatogram of sample 2 (Fig. 2) was due to the fact that the content of the methylene blue in its various preparations may vary within wide limits, ie. 60–98%. The dye is very sensitive to oxidation, and oxidation products (such as azure

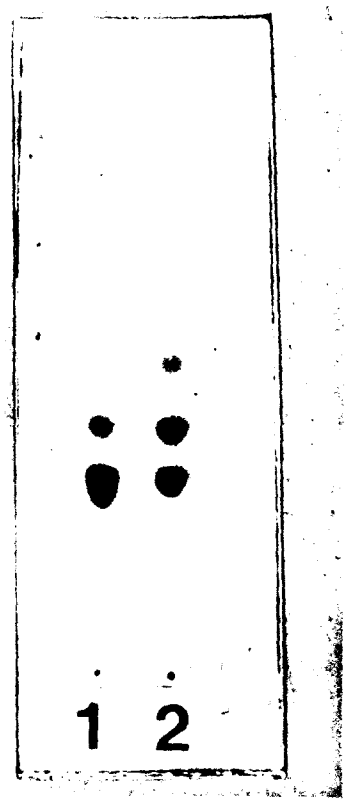


Fig. 2. TLC chromatogram of sample 2:
1. Methylene blue as reference substance
2. Sample 2

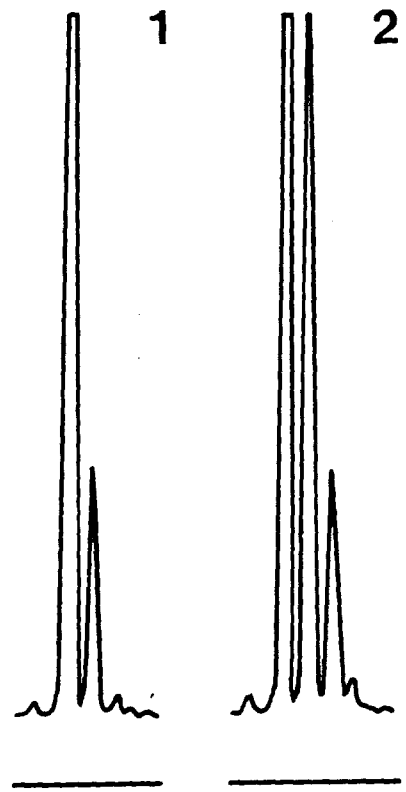


Fig. 3. Densitogram of sample 2:
1. Methylene blue as reference substance
2. Sample 2

B, azure C and others) are present as impurities.[25] The pure dye is represented by the highest peaks in Fig. 3. The calculated content of pure dye in sample 2 was 45%; in the standard it was 81.5%. The pink dye (in a small quantity) was found only in sample 1. Its R_f-value was higher than the R_f-values of the blue dyes. The same pink colour was obtained after the treatment of a leather sample with 5% HCl (H_2SO_4) and it appeared on the border between the two spots of a saturated solution of $K_2Cr_2O_7$ in 5% HCl (H_2SO_4) and solution of methylene blue in 5% HCl (H_2SO_4) on a filter paper. It was assumed from both experiments that the tanning agent Cr^{+3} was liberated from the leather by the action of HCl (H_2SO_4). An oxidation of Cr^{+3} to Cr^{+6} occurred. The methylene blue was oxidized by Cr^{+6} into a pink-coloured product in the acid medium. The same result could be obtained under other conditions and with other oxidizing agents, but possibly the acid medium is also important. From the 1930s there are recipes for linseed oil lacquers that include strong H_2SO_4 (66° Bé).[17] This supports our conclusion that the binding media of the upper layer of the leather coating are of linseed oil.

Finally, the pink dye could be accepted as an oxidized product of the methylene

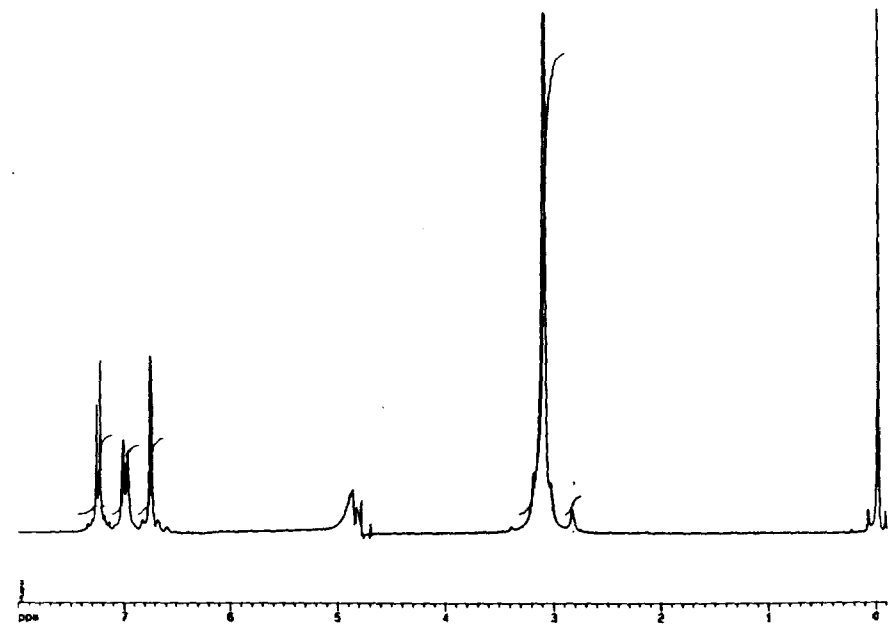


Fig. 4. ^1H NMR spectrum of the dye (methylene blue) extracted from the leather.

blue obtained in the course of preparing the original lacquer, and not necessarily an additional dye used to achieve the desired colour.

A last analytical result was found after mixing samples 1 and 2. The combined sample was separated by preparative TLC. Only the band with an R_f-value equal to the R_f-value of pure methylene blue was eluted from the TLC chromatogram and used for further examination. The final purification of the isolated dye was performed by gel chromatography on Sephadex LH-20.

The structure of the isolated pure dye from the leather coating was finally confirmed by ^{1}H NMR analysis. In the ^{1}H NMR spectrum of the dye we observed two doublets at δ 7.24 (d, 2H, J=9.6 Hz) and δ 6.97 (d, 2H, J=2.8 Hz) as well as one doublet of doublets at δ 7.03 (dd, 2H, J_1=2.8 Hz, J_2=9.6 Hz) for 6 aromatic protons in the structure of the isolated dye. Both $N(CH_3)_2$ groups are registered as 12 protons singlet at δ 3.11 (Fig. 4). The ^{1}H NMR spectrum of the dye is identical with that of methylene blue. The dye was thus definitely identified as methylene blue.

Conclusion

The results of the investigation proved that the leather of the gospel-book binding was chrome-tanned. Its colour coating contains two layers. The binding media of the first one are nitrocellulose. The upper layer contains linseed oil. The colour substance of both layers is methylene blue. The original coating was preserved in the areas under the silver applications and in the bands of the leather under the fly-leaves. In the other parts of the leather it was rubbed out to a large degree.

In accordance with the original technology of its manufacturing and with recipes from the period of the object's dating, we assume two blue finishes for the colour unification of the leather. The recipes are as follows (numbers in weight units, e.g. g).

1. First finish with nitrocellulose as the binding media:

nitrocellulose	1000
amylacetate	4000
acetone	3000
ethyl alcohol	1000
dibutyl phtalate	250
castor oil	750
titanium oxide	200
methylene blue	40

The nitrocellulose is dissolved in 3000 amylacetate and 2000 acetone. The castor oil and the titanium oxide are mixed separately. The whole quantity of dibutyl phtalate and the rest of the amylacetate are added subsequently. This mixture is added to the nitrocellulose solution. Finally the finish is dyed with methylene blue dissolved in the ethanol and the rest of acetone. The finish is brushed onto the cleaned surface of the leather.

2. Second finish with linseed oil as the binding media:

mature pure linseed oil	ca. 1000 (11)
white lead, $PbCO_3 . Pb(OH)_2$	5
lead sugar, $Pb(CH_3COO)_2 .3H_2O$	10
Berlin blue, $Fe_4[Fe(CN)_6]_3$	25
titanium oxide, TiO_2	30
methylene blue	10

The linseed oil is boiled at 250°C for 3–4 hours. The siccatives are added one after the other at intervals of 30 min at 200°C. The temperature is raised again and kept at 260–280°C until a thread with a length of 20–30 cm can be drawn from a sample of the mixture, which is cooled on a piece of glass. The titanium oxide and methylene blue are mixed with ethanol to form a paste. This mixture is stirred into the boiled linseed oil which has previously been cooled to 50°C. The homogeneous mixture is diluted with benzine and turpentine (1:1) until a thickness of 0.90 Bé is achieved. The finish is filtered though gauze or a metal screen. It is matured at 30–40°C for about 20 days. The finish is diluted again with a mixture 1:1 of benzine and turpentine and applied to the nitrocellulose coating in a thin layer with a velvet tampon or a fine brush.

Acknowledgements

The authors are indebted to Dr Nedyalka Dasskalova, Institute of Inorganic Chemistry, Bulgarian Academy of Sciences, for the measuring of the emission spectra.

Summaries

Ascertainment of the Original Technology for Manufacturing Leather Used for Gospel-Book Binding

An analysis was made of the leather cover of a gospel-book that had been submerged in a river for some days. The findings showed chrome-tanning, double coating with nitrocellulose and with linseed oil, and a dye of methylene blue. This accords with historical information on the making of gospel-books in Bulgaria and with the development of leather technology in this country in the period 1925

1945. On the basis of the experiment results and of formulas for leather coatings from that period, recipes are given that may be useful in the conservation finishing of leather binding.

Vérification de la technologie originale pour fabriquer le cuir utilisé pour la reliure d'un Evangéliaire

On a analysé le cuir de la couverture d'un Evangéliaire qui avait été immergé dans une rivière pendant quelques jours. Les résultats donnent un tannage au chrome, un double enduit avec nitrocellulose et huile de lin et un colorant au bleu de méthylène. Cela correspond aux données historiques sur la réalisation des Evangéliaires en Bulgarie et aux développements de la technologie du cuir dans cette région dans la période 1925–1945. Sur la base de résultats expérimentaux et de formules d'enduit pour le cuir de cette même période, on donne des recettes qui peuvent être utiles lors de la restauration de reliures en cuir.

Ermittlung der Herstellungsmethode des Einbandleders eines Evangeliars

Das Leder eines Evangeliars, welches einige Tage lang im Wasser eines Flusses gelegen hatte, wurde analysiert. Chromgerbung, eine zweifache Beschichtung, eine auf der Basis von Nitrocellulose, die andere mit Leinöl und Methylenblau als Farbstoff wurden nachgewiesen, was der Herstellungsweise von Büchern dieser Art und von Leder in Bulgarien im zweiten Viertel unseres Jahrhunderts entspricht (1925–1945). Aufgrund der Feststellungen und von Angaben aus dieser Zeit werden Rezepte mitgeteilt, die nützlich sein mögen für die Konservierung des Einbandleders.

REFERENCES

1. Larsen, R.: *Microchemical determination of vegetable tannins.* Leather Conservation News 7(1) (1990): 6–7.
2. Stahl, E.: *Dünnschicht-Chromatographie. Ein Laboratoriumshandbuch* [Thin-layer chromatography. Laboratory handbook]. Berlin: Springer Verl., 1967.
3. Beresova, T. T.: *Rakovodstvo k laboratornim zanyatiam po biologicheskoi chimii* [Laboratory handbook of biological chemistry]. Moscow: Medicina, 1976 (in Russian).
4. Zagorchev, B. N.: *Analitichna chimia* [Analytical chemistry]. Sofia: Technika, 2nd edition, 1972 (in Bulgarian).
5. Velcheva, M. P., Lekova, K. I., Slavcheva, N. N., Vladovska, Y. B. & Kosstadinov, K. K.: *Study of volatile organic compounds and lipids in the culture medium of methylomonas sp.* Comptes rendus de l'Académie bulgare des Sciences 37, 11 (1984): 1501–1504.
6. Sykes, R. L.: *The principles of tanning.* In: Calnan, C. & Haines, B., eds: Leather – its composition and changes with times. Northampton: The Leather Conservation Centre, 1991: 10.
7. Pesheva-Tzacheva, M. K.: *Control na kachestvito na gotovite koji* [Control of the quality of leather]. Sofia: Vish Chimico Technologicheski Institute, 1980 (in Bulgarian).
8. Patents: USSR 1969 (no. 234598), France 1970 (no. 2042206), India 1970 (no. 1911), Germany 1971 (no. 2012658), USA 1974 (no. 3852431) and 1976 (no. 3938951).
9. Metelkin, A. N. & Russakova, N. T.: *Titanovoe dublenie* [Titanium tanning]. Moscow: Lehkaja Industria, 1980 (in Russian).
10. Pesheva, M.: *Chimia i phisika na surovata koja i dabilnite vestestva* [The chemistry and physics of raw hide and of tanning materials]. Sofia: Vish Chimico Technologicheski Institute, 1982 (in Bulgarian).
11. Mayer, R.: *The artist's handbook of materials and techniques.* New York: The Viking Press, 4th edition, 1985.
12. Wehlte, K.: *Werkstoffe und Techniken der Malerei* [Materials and techniques of the art of painting]. Ravensburg: Otto Maier 1976.
13. Mutaffchiev, A.: *Fabrikacia na shevra, velur i boksove, koji za rakavitzi i lakove* [Production of chevreaux, suède, box-calf and leather for gloves and patent leather]. Sofia: 1933 (in Bulgarian).
14. Shapiro, A. E.: *Pokrivnie kraski i ich primenenie v kojepromishlenosti* [Dye coatings and their application in the leather industry]. Moscow: Lehkaja Industria, 1933 (in Russian).
15. Private communication, kindly given by Dr. B. Dimitrov, Director of the National Museum of History in Sofia.
16. Thomson, R. S.: *Surface coating and finishes.* In: Calnan, C. & Haines, B. (cf. Ref. 6): 34–37.
17. Pchelin, A. A.: *Lakirovanie koji* [The varnishing of leather]. Moscow: Lehkaja Industria, 1937 (in Russian).
18. Scheiber, J.: *Kombinationslacke* [Combined laquers]. Farbe und Lack 17 (1928).
19. Antonov, V. K.: *Chimia proteolisa* [The chemistry of proteolysis]. Moscow: Nauka, 1983 (in Russian).
20. Makes, F.: *Enzymatic consolidation of the portrait of Rudolf II as "Vertumnus" by Giuseppe Archimboldo with a new multi-enzyme preparation isolated from Antarctic krill (Euphausia superba).* Göteborg Studies in Conservation 1 (1988): 46.
21. Landmann, A. W.: *Lubricants.* In: Calnan, C. & Haines, B. (cf. 6): 26–28.
22. Nikolski, B. P., Grigorov, O. N., Pozyn, M. E., Poray-Koshitz, B. A., Rabinovich, W. A., Rachinski, F. J., Romankov, P. G. & Friedrichsberg, D. A.: *Spravochnik chimika* [Handbook for chemists] Vol. II. Leningrad: Gostchimizdat, 2nd edition, 1963 (in Russian).
23. Chernov, N. W., Arronina, J. N., Gaydarov, L. P., Goloweeva, A. N., Strahov, I. P. & Shesstakova, I. S.: *Technologia koji* [Leather technology]. Moscow: Lehkaja Industria 1952 (in Russian).
24. Otto, G.: *Das Färben des Leders. Theorie und Praxis der Lederfärberei* [Leather dyes. Theory and practice of leather dyeing]. Darmstadt: Rother 1964.
25. *Thiazine dyes.* Merck Spectrum, 1 (1993): 18–19.

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Permanence of Paper in Polish Books of the Period 1900–1994

by BRONISŁAW ZYSKA

Introduction

It is clear to everyone that there is a need for the mass deacidification of books and archival materials published during the XIXth and XXth century, printed on acid paper, in order to rescue the cultural heritage of the nation.

One of the main steps in the organization of the deacidification of books of the XIXth and XXth century in Poland is the investigation of the actual permanence of paper, performed on library collections.

The best example of such investigations are the papers published by William James Barrow in the series of publications in the period 1963–1969.[1] Those investigations were rediscovered ten years after W. J. Barrow's death in the year 1978 by Pamela W. Darling and Sherelyn Ogden.[2] The statement by both scientists on the subject of the hazard to the American library collections, published in the years 1900–1939, is still of great value and has to be cited. It was then stressed that:

- 40% of books published in the years 1900–1939 will have deteriorated within 25 years;
- 40% of books from this period may be used over a period of 50 years and
- only 20% of books from the period 1900–1939 will last past the year 2010.

Since 1983, several reports have been published in the USA dealing with the evaluation of paper permanence in books, including studies at the Wilson Library, University of North Carolina, at the Yale University Library, at the Syracuse University Libraries, at the Local History and Genealogy Collection of the New York Public Library and the Library of the University of Illinois at Urbana–Champaign. The libraries mentioned collected a total of 14.4 million volumes, of which 4.0 million volumes were printed on book paper that is now very brittle.[3]

Similar investigations were undertaken in West Germany in 1988 on behalf of the Deutsches Bibliotheksinstitut, in 54 scientific libraries, which collected 82.6 million volumes altogether. A sample of 7110 volumes was taken from those libraries in which, among other parameters, the paper performance was tested. U. Usemann-Keller[4] reported that 12% of the volumes had been printed on good paper that was now very brittle and broke after 3 double folds, done manually. On the basis of the investigation it was concluded that of 152 million volumes in German scientific libraries, 18 million cannot be rescued even by mass deacidification because of the brittleness of the pages. The paper performance in books and archival materials was also investigated in West Germany in 1992 by Peter Zeisler, Udo Hamm and Lothar Göttsching.[5] The research activity on the evaluation of paper permanence in library collections performed in the USA and West Germany is of the greatest value in the estimation of hazard to libraries due to acid paper.

Similar investigations have been undertaken at the Institute of Library Sciences, Silesian University, in Katowice. Preliminary results have been published since 1988 and have dealt with the following fragments of book collections:

- 64 volumes of XIXth century Silesian prints;[6] preliminary results of the folding endurance in 303 volumes of Polish books from the period 1810–1980;[7]
- pH and folding endurance in 121 Polish volumes from the period 1960–1979, as well as their classification according to the five groups of permanence of William James Barrow;[8]
- pH and folding endurance in 43 Polish prints of the period 1861–1870;[9]
- pH and folding endurance in 111 books and pamphlets printed in Cieszyn, dating from the period 1818–1910, as well as their classification according to William James Barrow;[10]
- the permanence of printing paper in 49 volumes of the Polish biographical dictionary from the period 1977–1992, including their classification according to William James Barrow;[11]
- the permanence of printing paper in 142 books and pamphlets printed in Cieszyn, dating from the period 1860–1939, as well as their classification according to William James Barrow;[12]
- the permanence of printing paper in 1026 volumes of Polish books, dating from the periods 1810–1909, 1920–1939 and 1950–1994, as well as their classification according to William James Barrow.[13]

This article presents the evaluation of book paper performance in 1395 volumes of Polish books dating from the period 1900–1994. To evaluate the process of book paper deterioration, estimation of the pH and folding endurance were selected as test properties. The significance of the folding test was categorized

according to the method conceived by William James Barrow in 1959. In the statistical analysis of results the single linkage method was used according to the formula of Lance-Williams.[18 22]

Material and Methods

A total of 1395 Polish books from the period 1900–1994 were chosen for testing. Table 1 presents the data for books investigated. They were divided into consecutive decades, starting from 1900–1909. In the decades 1900–1909, 1910–1919 and 1940–1949 the number of investigated books is very low, because it was difficult to collect a larger amount of copies from those periods. The decade 1940–1949 is represented only by books printed in the period after World War II, i.e. from the period 1946–1949. The publishing of Polish books during World War II was absolutely forbidden by the Nazis. Differences in the number of books tested for folding endurance and pH results from the fact that sometimes the three parameters could not be tested simultaneously, i.e. folding endurance in machine direction and cross direction, and pH.

Folding endurance

Folding endurance tests were performed on Schopper apparatus according to the Polish standard PN-73/P-50134.[14] The size of the samples was 10×1.5 cm, cut

Table 1. Polish books investigated for the permanence of printing paper, dating from the period 1900–1994

Decade	Total no. of books	No. of books tested for		
		folding endurance		pH
		MD	CD	
1900–1909	69	48	48	68
1910–1919	38	32	30	37
1920–1929	137	125	73	137
1930–1939	173	164	106	173
1940–1949	31	26	30	29
1950–1959	307	255	297	307
1960–1969	184	135	139	177
1970–1979	165	130	130	152
1980–1989	154	148	146	146
1990–1994	137	126	122	137
Total	1395	1189	1121	1363

from the margins of paper, parallel with and perpendicular to the line of printing. Up to 10 samples were tested for each direction, i.e. the machine and cross direction. In the series of 10 results, the fifth result was chosen as median. The standard tension of 1 kG was used in the estimation of folding endurance. The moisture of book paper at testing was 8–10%.

pH measurements

pH was measured by a cold extraction method according to BS 4971: Part 1: December 1973[15] and Polish standard PN-84/P-50109[16], using pH meter type OP-205/1 Radelkis (Hungary) with Radelkis Universal Electrode. The weight of paper samples was 1±0.01 g.

Classification of book paper permanence

In our investigations, to categorize the durability of books from the period 1900–1994, we used the classification of William James Barrow, published in 1959 in his book "Deterioration of Book Stock. Causes and Remedies".[17] The details are given in Table 2.

Statistical analysis of results by clustering of data or cluster analysis can be used for multivariate analyses. A classical example is when an investigator groups the cases according to features. Details are given by J. E. Mezzich and H. Solomon[18], J. E. Overall and C. J. Klett[19], S. C. Johnson[20], P. R. Kreishnaiah and L. N. Kanal[21] and R. G. Brereton.[22]

In the statistical analysis of results the single linkage method was used according to the formula of Lance-Williams. The first group of features are the average and median of double folds of paper samples in machine direction, average and median of double folds in cross direction and the pH of paper, in all, five features. The objects from 1 to 10 represent the decades: 1900–1909, 1910–1919, 1920–

Table 2. Classification of the permanence of books according to William James Barrow

Class	No. of double folds	Strength of the book paper	Permanence of books in years
1	0–3	very weak	at moderate use under 25
2	4–24	low	25
3	25–75	medium A	25–50
4	75–200	medium B	over 50
5	over 200	high	marked durability

1929, 1930–1939, 1940–1949, 1950–1959, 1960–1969, 1970–1979, 1980–1989 and the five year period 1990–1994.

As the second group of features, four in all, data connected with the pH of paper were chosen: minimum pH, average pH, median pH and maximum pH. Book papers with a pH over 5.9 have been excluded from that analysis. There were 27 samples out of the total of 1363 in the whole period 1900–1994.

Results

Folding endurance

Table 3 presents the results of folding endurance in the machine direction as well as in the cross direction, given as the median of number of double folds for each decade between 1900 and 1994. For each direction and each decade the medians are presented as the minimum, middle and maximum median of number of double folds. The most important figures in Table 3 are the middle medians. As can be seen, in the period 1900–1959 the middle median of double folds varies in the machine direction between two and three folds and in the cross direction between one and two folds. A slight increase can be observed in double folds in both directions for the period 1960–1979. A remarkable and justified increase of the middle median for the period 1980–1994 can also be observed.

Table 3. Number of double folds of the paper in Polish books dating from the period 1900–1994

Decade	Median of number of double folds					
	minimum		middle		maximum	
	MD	CD	MD	CD	MD	CD
1900–1909	0	0	3	2	12	5
1910–1919	1	1	3	1	8	3
1920–1929	0	0	2	1	20	8
1930–1939	0	0	2	1	11	7
1940–1949	0	0	2	1	19	8
1950–1959	0	0	2	2	33	28
1960–1969	1	0	4	3	28	17
1970–1979	1	0	5	3	49	30
1980–1989	1	0	10	5	135	103
1990–1994	2	1	60	24	323	108

Table 4. pH of paper in Polish books dating from the period 1900–1994

Decade	No. of books	The pH of paper			No. of books with paper pH over 6.0
		minimum	median	maximum	
1900–1909	68	2.70	4.73	5.60	0
1910–1919	37	2.90	4.73	5.62	0
1920–1929	137	3.80	4.81	9.01	7
1930–1939	173	3.82	4.99	6.88	2
1940–1949	29	4.07	4.60	7.41	1
1950–1959	307	3.91	4.79	5.85	0
1960–1969	177	4.09	4.96	7.60	3
1970–1979	152	4.35	5.10	7.70	5
1980–1989	146	3.98	5.06	7.84	4
1990–1994	137	4.49	5.25	6.53	5
Total	1363	–	–	–	27

pH of paper

Table 4 presents the results of the pH of paper measured by a cold extraction method given as medians for each decade of the period 1900–1994. The medians are presented as the minimum, middle and maximum median of paper in books tested.

The variation of the middle median of pH of paper is very low in the period 1900–1969. During the period 1970–1994 a small increase of pH over the value of pH 5.0 was observed. Of the total number of 1363 volumes tested, only in 27 volumes was the pH higher than 5.9. Those measurements will be discussed in future investigations.

Classification of book paper permanence

Table 5 presents the results of the book paper permanence according to the classification of William James Barrow. As can be seen for the period 1900–1979, in consecutive decades 93–100% of volumes were made of paper categorized as of the first and second class of permanence. In the first class of permanence, from 25% of volumes from the decade 1970–1979 to 83% of volumes from the decade 1900–1909 have been classified. In the decade 1980–1989 and in the years 1990–1994, changes in the classification are evident, as the percentage of books in the first class of permanence amounts here to 7% in the period 1980–1989 and only 1% in the years 1990–1994.

Table 5. Classification of the permanence of book paper in Polish books in the period 1900–1994

Decades	No. of books / %	Strength of book paper: Very weak	Low	Medium A	Medium B	High	Total
1900–1909	No. of books	40	8	0	0	0	48
	%	83.33	16.67	0.00	0.00	0.00	100.00
1910–1919	No. of books	25	7	0	0	0	32
	%	78.12	21.88	0.00	0.00	0.00	100.00
1920–1929	No. of books	103	22	0	0	0	125
	%	82.40	17.60	0.00	0.00	0.00	100.00
1930–1939	No. of books	135	29	0	0	0	164
	%	82.32	17.68	0.00	0.00	0.00	100.00
1940–1949	No. of books	15	11	0	0	0	26
	%	57.69	42.31	0.00	0.00	0.00	100.00
1950–1959	No. of books	187	65	3	0	0	255
	%	73.33	25.49	1.18	0.00	0.00	100.00
1960–1969	No. of books	63	71	1	0	0	135
	%	46.67	52.59	0.74	0.00	0.00	100.00
1970–1979	No. of books	33	88	9	0	0	130
	%	25.38	67.69	6.92	0.00	0.00	100.00
1980–1989	No. of books	11	102	24	11	0	148
	%	7.43	68.92	16.22	7.43	0.00	100.00
1990–1994	No. of books	2	22	65	52	3	144
	%	1.39	15.28	45.14	36.11	2.08	100.00
1900–1994	No. of books	614	425	102	63	3	1207
	%	50.87	35.21	8.45	5.22	0.25	100.00

Cluster analysis of results

Table 6 gives the raw data for the cluster analysis for 10 objects and five features. Table 7 comprises the Euclidean distances for nine clusters, basing on the data from Table 6. The Euclidean distances of succeeding clusters are presented in Fig. 1. As can be noted, the closer this distance is to zero, the more similar the

Table 6. Raw data for cluster analysis of double folds and pH of book paper in the period 1900–1994

Objects		Average double folds: MD average	MD average median	CD average	CD average median	Average pH
		Features				
Decades	No	1	2	3	4	5
1900–1909	1	2.33	2.60	1.67	1.71	4.59
1910–1919	2	2.69	2.81	1.72	1.73	4.59
1920–1929	3	2.62	2.59	1.91	1.82	4.82
1930–1939	4	2.38	2.37	1.50	1.52	4.91
1940–1949	5	4.38	4.27	2.71	2.53	4.73
1950–1959	6	4.41	3.89	2.99	2.86	4.80
1960–1969	7	8.89	5.72	5.26	3.67	4.98
1970–1979	8	13.28	8.82	7.08	5.30	5.13
1980–1989	9	22.93	20.91	10.06	10.49	5.13
1990–1994	10	75.44	71.37	35.91	32.03	5.29

Table 7. Clusters calculated by the single linkage method based on data from Table 6

No. of the cluster	Subclusters		Euclidean distance
Cluster 1	Object 1	Object 2	0.001420
Cluster 2	Cluster 1	Object 3	0.002630
Cluster 3	Object 5	Object 6	0.003280
Cluster 4	Cluster 2	Object 4	0.003489
Cluster 5	Cluster 4	Cluster 3	0.010905
Cluster 6	Cluster 5	Object 7	0.022135
Cluster 7	Cluster 6	Object 8	0.024206
Cluster 8	Cluster 7	Object 9	0.067106
Cluster 9	Cluster 8	Object 10	0.332208

objects are. Let us present the calculations of the Euclidean distances on the basis of analyzed features of book paper (double folds and pH) in decades as objects.

The most similar objects are the paper of books made in the decades 1900–1909 and 1910–1919. Close to book paper quality from the period 1900–1919 is

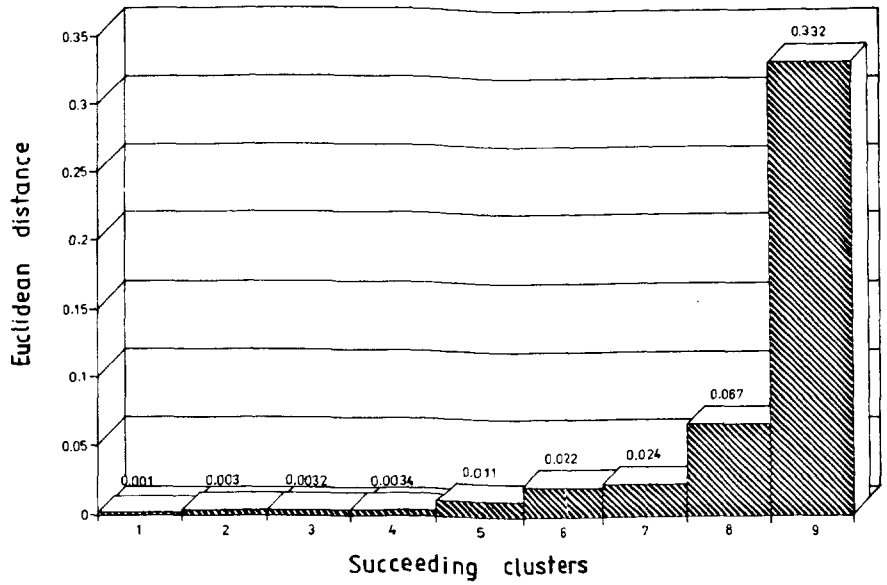

Fig. 1. Cluster analysis of double folds and pH of book paper in the period 1900–1994.

that of book paper from the decade 1920–1929. The next (cluster 3) is the book paper of the decades 1940–1949 and 1950–1959.

Cluster 4 represents the book paper of the period 1900–1929 and the decade 1930–1939.

Cluster 5 encloses the features of book paper of the period 1900–1939 and the two decades 1940–1959, having, as cluster 4 does, the Euclidean distance of 0.010905.

Cluster 6 encloses the features of book paper from the decades 1900–1959 and the decade 1960–1969; while cluster 7 is very similar to cluster 6, when the features of book paper of the decades 1900–1969 are included the decade 1970–1979. The book paper from decade 1980–1989 (object 9) and the 5-year period 1990–1994 (object 10) differ greatly in the levels of double folds. For such reasons, cluster 8 includes data of the period 1900–1979, the decade 1980–1989 has the value of the period 1900–1979, the decade 1980–1989 has the value of the Euclidean distance of 0.067106, while cluster 9 includes data of the period 1900–1989 and the 5-year period 1990–1994, having a very high Euclidean distance, 0.332208.

Looking at Tables 5 and 6 one may note that in the decades between 1900 and 1979 the permanence of book paper was very low and it decreased even further in the next decades. Because of low pH, the forecast for the permanence of the book paper of the period 1980–1994 is also rather negative.

Table 8. Raw data for cluster analysis of pH of book paper in the period 1900–1994[a]

Objects		pH of book paper			
Decades	No	minimum	average	median	maximum
1900–1909	1	2.70	4.59	4.73	5.60
1910–1919	2	2.90	4.59	4.71	5.62
1920–1929	3	3.80	4.71	4.69	5.75
1930–1939	4	3.82	4.89	4.99	5.80
1940–1949	5	4.07	4.63	4.59	5.45
1950–1959	6	3.91	4.80	4.79	5.85
1960–1969	7	4.09	4.95	4.93	5.80
1970–1979	8	4.35	5.05	5.00	5.85
1980–1989	9	3.98	5.06	5.03	5.97
1990–1994	10	4.49	5.25	5.24	5.92

[a]Values of pH 6.0 or higher have been excluded.

Because of the importance of the influence of book paper pH on its permanence, the cluster analysis of the pH of book paper over the whole period 1900–1994 was done. The raw data for such an analysis have been given in Table 8. Values of the pH of book paper of 6.0 or higher have been excluded from this table. Books with this higher book paper pH will be separately investigated in the future. As mentioned before, 27 books were included in this cluster. Table 9 presents the Euclidean distances for nine clusters, calculated on the basis of four features (Table 8) for 10 objects, i.e. nine decades of the period 1900–1989 and the 5-year period 1990–1994. The Euclidean distances of consecutive clusters are shown in Fig. 2.

Table 9. Clusters calculated by the single linkage method based on data from Table 7

No. of the cluster	Subclusters		Euclidean distance
Cluster 1	Object 3	Object 6	0.002180
Cluster 2	Object 7	Object 9	0.002569
Cluster 3	Cluster 1	Object 4	0.002581
Cluster 4	Object 1	Object 2	0.002638
Cluster 5	Cluster 3	Cluster 2	0.003134
Cluster 6	Cluster 5	Object 8	0.003661
Cluster 7	Cluster 6	Object 10	0.003750
Cluster 8	Cluster 7	Object 5	0.004589
Cluster 9	Cluster 4	Cluster 8	0.011928

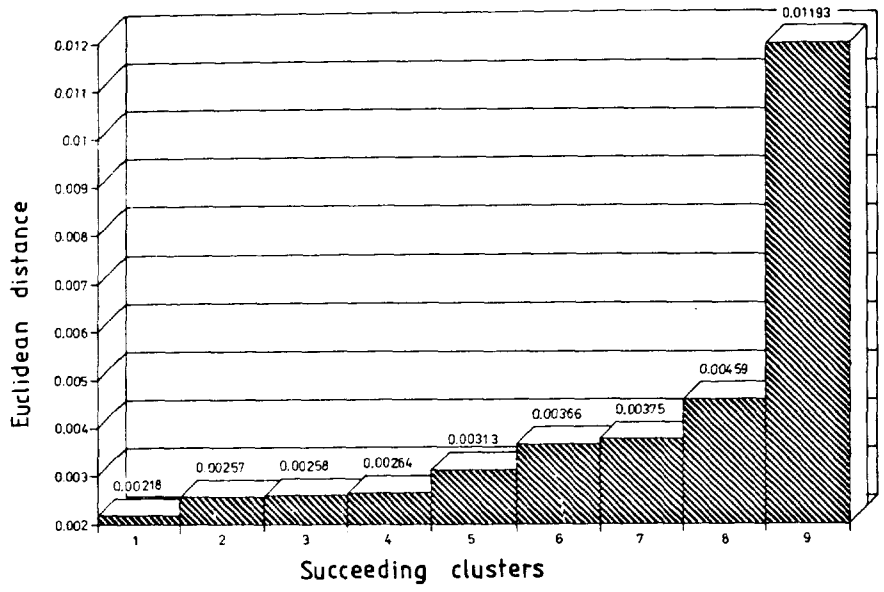

Fig. 2. Cluster analysis of pH of book paper in the period 1900–1994.

Let us present the calculations of the Euclidean distances on the basis of analyzed features of the book paper, i.e. minimum, average, median and maximum pH, in the period 1900–1994, divided into 10 objects.

The most similar objects, from the point of view of the pH of book paper, are represented by the decades 1920–1929 and 1950–1959. This statement is very important as it proves the similarity of book paper pH in two different historical periods, i.e. for books printed before World War II and books printed after it. Close to the book paper of the above two decades in terms of permanence, is the book paper of the decades 1960–1969 and 1980–1989, grouped as cluster 2. The same applies to cluster 3, which includes the book paper of the decade 1930–1939. In cluster 4 we have the book paper of the decades 1900–1909 and 1910–1919. The similarities in the acidity of book paper may be noted as far as cluster 9. The values of the Euclidean distances are in all the decades, i.e. objects, very low, demonstrating that the differences in pH are very small throughout the whole period 1900–1994. This is the evidence of the very poor permanence of book paper used in publishing in the period 1970–1979 and of the decrease in the strength of book paper during the period 1980–1994.

CONCLUSION

This study is devoted to the estimation of the permanence of paper in 1395 Polish books of the period 1900–1994. The following features were selected for the evaluation of the permanence of paper: the folding endurance tested on Schopper apparatus and the pH measurements by a cold extraction method. The durability of the paper was categorized according to the classification of William James Barrow. For multivariate analysis of the measured features over the period 1900–1994, divided into decades, the method of cluster analysis was chosen, with the aim of applying the single linkage method, according to the Lance-Williams formula.

In the period 1900–1959 the middle median of double folds varies for the machine direction, between two and three folds, and for the cross direction between one and two folds. In the decades 1960–1969 and 1970–1979 a small increase in double folds in both directions could be observed. The data for double folds on paper in books printed in the period 1980–1994 obviously cannot be considered. The middle median of the pH of paper varies in the period 1900–1969 between 4.60 and 4.99. In the decades 1970–1979 and 1980–1989 the middle median pH of paper is of the 5.06–5.10 level, and for the period 1990–1994 it amounts to 5.25. For the period 1900–1979, in consecutive decades, from 93 to 100% of volumes were made of paper the permanence of which is categorized as first or second class according to W. J. Barrow's classification.

Cluster analysis may be used in the investigation of the book paper permanence as a very interesting method of evaluation of the properties of paper, but always in comparison with the consecutive decades of the period 1900–1994.

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Summaries

Permanence of Paper in Polish Books of the Period 1900–1994

The study is devoted to the estimation of the permanence of paper in 1395 Polish books of the period 1900–1994. As features for the evaluation of the permanence of paper, the folding endurance and the pH measurements by a cold extraction method have been chosen. Categorization of the durability of the paper was undertaken according to the classification of William James Barrow 1904–1967. For multivariate analysis of the measured features over the period 1900–1994, divided into decades, the method of cluster analysis was chosen, applying the single linkage method, according to the Lance-Williams formula.

For the period 1900–1979 in consecutive decades, from 93 to 100% of volumes were made of paper the permanence of which is categorized as first or second class, according to W. J. Barrow's classification.

Permanence du papier de livres polonais datant de la période 1990–1994

Cette étude a pour objet l'évaluation de la permanence du papier de 1395 livres polonais datant de la période 1900–1994. Les tests choisis pour évaluer la permanence du papier sont la résistance au pli et la mesure du pH après extraction à froid. On a établi des catégories de durabilité du papier selon la classification de William James Barrow 1904–1967. Pour l'analyse multivariée des mesures effectuées pour la période 1900–1994, par période de dix ans, on a choisi la méthode des clusters appliquant la méthode de correspondance simple selon la formule Lance-Williams.

Pour la période 1900–1979, en décennies consécutives, de 93 à 100% des volumes sont composés de papier dont la permanence est considérée comme première ou deuxième classe selon la classification de W. J. Barrow.

Die Alterungsbeständigkeit der Papiers in Polnischen Büchern aus der Zeit 1900 bis 1994

Die Studie gilt der Abschätzung der Alterungsbeständigkeit des Papiers in polnischen Büchern aus der Zeit 1900 bis 1994. Als Abschätzungskriterien wurden Falzzahl und pH (Kaltextrakt) gewählt. Die Papiere wurden entsprechend der Klassifizierung von W. J. Barrow in fünf Qualitätsstufen eingeteilt. Als Multivarianz-Analyse der gemessenen Eigenschaften wurde, in Einteilung nach Dekaden 1900–1994, die Cluster-Analyse mit Einfachverknüpfung nach der Lance-Williams-Formel gewählt.

93–100% der zwischen 1900 und 1979 hergestellten Bücher gehören in die unterste oder die zweitunterste Klasse der Barrow'schen Einteilung.

References

1. Barrow, W. J.: *Permanence/durability of the book. I. A two-year research program.* Richmond, Virginia, 1963. *II. Test data of naturally aged papers.* Richmond, Virginia, 1964. *III. Spray deacidification.* Richmond, Virginia, 1964. *IV. Polyvinyl acetate (PVA) adhesives for use in library bookbinding.* Richmond, Virginia, 1965. *V. Strength and other characteristics of book papers, 1980–1899.* Richmond, Virginia, 1967. *VI. Spot testing for permanence/durability of book papers.* Richmond, Virginia, 1969.
2. Darling, P. W. & Ogden, S.: *From problems perceived to programs in practice: the preservation of library resources in USA, 1956–1980.* Library resources and technical services 25 (1981): 9–29.
3. Zyska, B.: *[On the permanence of book papers.]* Katowice: Instytut Biblioteknoznawstwa, 1993: 1–148 (English, German and Russian Summaries).
4. Usemann-Keller, U.: *Bestandschäden in deutschen Bibliotheken. Untersuchung von 0,01% der Bestände ausgewählter Bibliotheken der Bundesrepublik durch das Deutsche Bibliothekinstitut.* Zeitschrift für Bibliothekswesen und Bibliographie, Frankfurt/M (1989): 109–23.
5. Zeisler, P., Hamm, U. & Göttsching, L.: *Untersuchungen zum Zustand von Papier in Archiven und Bibliotheken.* In: Plasmann, E., Müller, H., Tussing, W., eds. Frankfurt am Main: 81. Deutscher Bibliothekartag in Kassel 1991. 1992: 55–74.
6. Zyska, B. & Pietraszek, E.: *[Permanence of nineteenth-century book papers in Silesia.]* Roczniki Biblioteczne, R. XXXII (1988): 293–306. (Russian and French summaries).
7. Zyska, B. J. & Jarosz, A. W.: *The awareness of conservation. Ten years of experience at the Silesian University, Katowice, Poland.* Restaurator 13 (1992): 138–47.
8. Zyska, B.: [*Permanence of the book paper of Polish books of the period 1960–1979. Bulletin No. 2.*] In: Żmigrodzki, Z., ed. Studie bibliologiczne 6 (1993): 140–6 (Russian and English Summaries).
9. Zyska, B. & Mrowiec, E.: *[The evaluation of the permanence of paper in the Polish prints from 1861–1870. Bulletin No. 3.]* In: Zyska, B., ed. Studia bibliologiczne 7 (1993): 123–30 (Russian and English Summaries).
10. Zyska, B. & Mrowiec, E.: *[Assessment of the permanence of paper in printed works from Cieszyn of the period 1818–1910. Bulletin No. 4.]* In: Zyska, B., ed. Studia bibliologiczne 8 (1994): 145–61 (Russian and English Summaries).
11. Zyska, B. & Lech, A.: *[Assessment of the permanence of print paper in the Polish Biographical Dictionary from the period 1977–1992. Bulletin No. 5.]* In: Zyska, B., ed. Studia Bibliologiczne 8 (1994): 162–71. (Russian and English Summaries).
12. Zyska, B.: *[Assessment of the permanence of Cieszyn prints from the period 1860–1939 and prospects of their saving.]* In: Panic, I., ed. *Z problemów ochrony, konserwacji i rejestracji regionalnego dziedzictwa piśmienniczego.* Panic, I., ed. Cieszyn: Książnica Cieszyńska, 1994: 7–26.
13. Zyska, B.: *[Acid paper. The hazard for XIXth and XXth century prints.]* Katowice: Wojewódzka Biblioteka Publiczna, 1995: 1–44. (English Summary).
14. Polish Standard PN-73/P-50134. *[Products of the paper industry. Estimation of folding endurance.]*
15. BS 4971: Part 1: December 1973. *A recommendation for repair and allied processes for the conservation of documents.* Appendix B. Method 1.
16. Polish Standard PN-84/P-50109 *[Products of the paper industry. Estimation of the pH of paper.]*
17. *Deterioration of book stock. Causes and remedies [1900–1949]. Two studies on the permanence of book paper.* Conducted by: Barrow, W. J. & Church, R. W., eds. Richmond, Virginia: The Virginia State Library, 1959: 1–68.
18. Mezzisch, J. E. & Solomon, H.: *Taxonomy and behavioral science.* New York: Academic Press, 1980.
19. Overall, J. E. & Klett, C. J.: *Applied multivariate analysis.* New York: McGraw-Hill, 1972.
20. Johnson, S. C.: *Hierarchical clustering schemes.* Psychometrica 32 (1967): 241–54.

21. Krishnaiah, P. R. & Kanal, L. N., eds.: *Handbook of statistics*. Vol. 2. Amsterdam: North-Holland, 1982.
22. Brereton, R. G.: *Chemometrics. Applications of mathematics and statistics to laboratory systems*. New York: Ellis Horwood, 1993: 1–307.

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Evaluation of Adhesives and Supporting Materials for the Process of Lamination of Old Documents

by D. G. SURYAWANSHI, P. M. SINHA & M. V. NAIR

Introduction

In the historical collections of the world, in our museums, archives, cultural institutions, private collections, etc, there are huge amounts of records on paper and other writing support material, such as parchment, papyrus, palm-leaf, and birch-bark. The problems of their preservation are enormous and various. One of the main problems is the lamination of very old and brittle objects.

The technique for laminating paper documents that is readily available at international level employs cellulose acetate foil and Japanese tissue paper. This method of lamination is very common, especially in archives. To some extent, the technique can also be used on objects of palm-leaf and birch-bark, but from the economic point of view this lamination technique is very expensive, and the materials are not always easily available, at least not in countries that are not fully industrialized. Therefore, at the Indian National Research Laboratory for the Conservation of Cultural Property (NRLC) in Lucknow, an experimental study has been undertaken to find alternative lamination techniques based on easily available and simple materials. Our study consisted of examining and experimenting with various adhesives in different percentages. As supporting materials, we used Nepalese handmade paper, Japanese tissue paper, Indian tissue paper, chiffon, and combinations of these materials. The quality and durability of these materials were defined according to their behaviour during accelerated ageing.

Experimental

The following materials were used.

Adhesives

- Carboxy methyl cellulose
- Methyl cellulose
- Maida (wheat flour)
- Dextrine
- A mixture of CMC and maida (1:2)
- A mixture of CMC and dextrine (1:2)

The adhesives were prepared in the concentration of 1.0, 1.5 and 2.0 percentages each, as dry material in distilled water.

Supporting Materials

- Nepalese handmade paper
- Japanese tissue paper
- Indian tissue paper

Table 1. Folding endurance of treated papers

Accelerated ageing		Nepalese handmade paper				Japanese tissue paper			
		0 h	24 h	48 h	72 h	0 h	24 h	48 h	72 h
	0%	788	723	628	614	180	172	116	102
Carboxy	1%	776	744	730	538	220	215	204	194
methyl	1.5%	723	712	684	493	222	217	199	131
cellulose	2%	786	747	549	384	202	198	183	158
Methyl	1%	528	512	473	432	310	291	235	198
cellulose	1.5%	528	505	435	318	311	289	232	148
	2%	526	510	432	301	310	280	223	129
Maida	1%	520	508	490	263	242	208	203	168
(wheat	1.5%	511	484	492	262	216	217	198	172
flour)	2%	514	488	489	264	236	214	200	162
Dextrine	1%	788	783	737	663	183	178	132	122
	1.5%	788	777	699	692	189	180	144	127
	2%	785	772	712	675	184	165	139	126
CMC	1%	591	578	552	508	242	242	216	184
and	1.5%	590	578	530	499	248	246	222	179
Maida	2%	591	577	532	500	246	245	218	180
CMC	1%	400	400	336	285	210	198	189	152
and	1.5%	402	398	322	280	208	198	174	141
Dextrine	2%	400	398	331	260	205	197	172	139

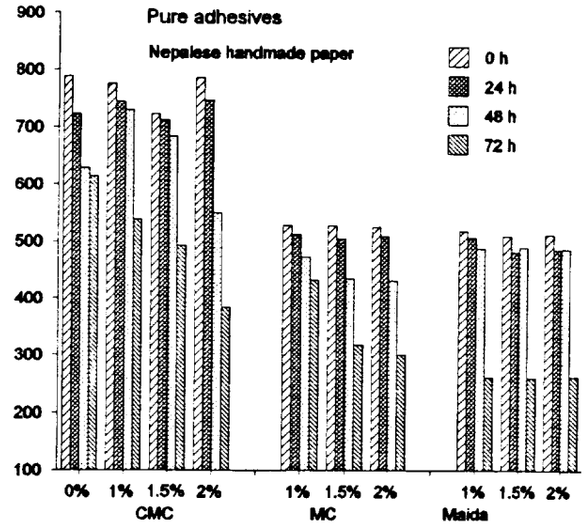

Fig. 1. Folding endurance before and after the accelerated ageing of Nepalese handmade paper treated with pure adhesives.

- Chiffon
- Chiffon and Indian tissue paper
- Chiffon and Japanese tissue paper
- Chiffon and Nepalese handmade paper
- Nepalese handmade paper and Indian tissue paper

Table 2. Folding endurance of combined materials

Accelerated ageing		Chiffon+Nepalese paper				Chiffon+Japanese tissue paper			
		0 h	24 h	48 h	72 h	0 h	24 h	48 h	72 h
Carboxy methyl cellulose	1–1.5–2%	higher than 2000 in all cases							
Methyl cellulose	1–1.5–2%								
Maida (wheat flour)	1–1.5–2%								
Dextrine	1–1.5–2%								
CMC and Maida	1–1.5–2%								
CMC	0%	higher than 2000 in all cases				>2000	>2000	>2000	>2000
and	1%					>2000	1820	1890	1836
Dextrine	1.5%					>2000	1820	1810	1822
	2%					>2000	1765	1745	1732

The supporting materials were cut into pieces of 24×16 cm. The adhesives in the above consistency were applied on the supporting materials which were kept on a thin polythene sheet on a smooth table. A fine sable-hair brush was used to apply the solutions over the surface of the supporting materials. This was done twice, resulting in two layers of adhesive. The assembly was left at room temperature overnight for drying.

The dried assembly of supporting material and adhesive layers was lifted up slowly and cautiously, prepared as standard sample specimens, and tested physically (folding endurance) and optically (brightness) according to the standard methods of the American Society for Testing and Materials (ASTM) and the Technical Association of the Pulp and Paper Industry (TAPPI). The same samples were aged by keeping them in oven at 105°C±2°C for 24, 48 and 72 hours. At each of these times, the brightness and folding endurance were measured. The results are given in Tables 1–2 and Figs 1–4.

For brightness a gloss/reflectance meter (AIM-66, manufactured by M/s AIM-IL, New Delhi, India) was used; for folding endurance the apparatus Köhler-Molin (M/s Lorentzen and Wetter, Stockholm, Sweden). The results before and after accelerated ageing are given in Tables 1–4.

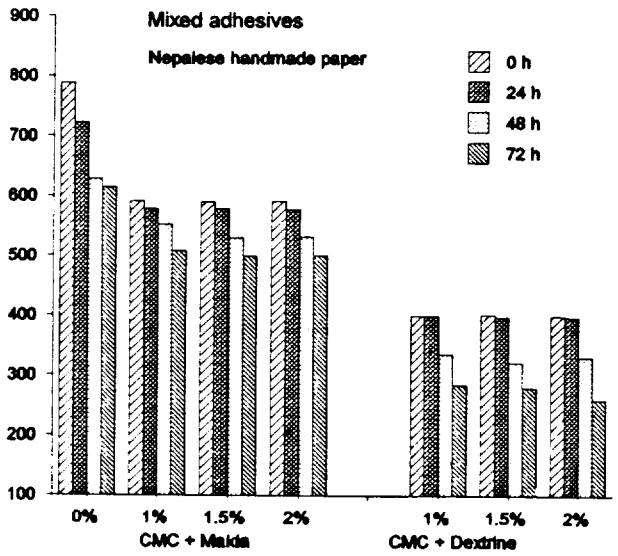

Fig. 2. Folding endurance before and after the accelerated ageing of Nepalese handmade paper treated with mixed adhesives.

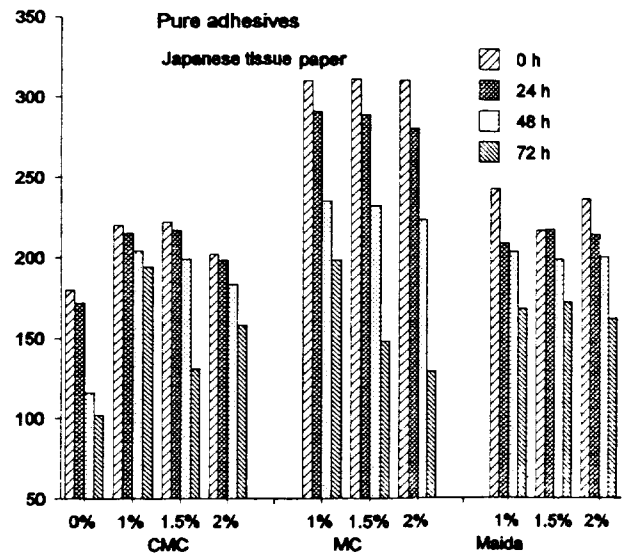

Fig. 3. Folding endurance before and after the accelerated ageing of Japanese tissue paper treated with pure adhesives.

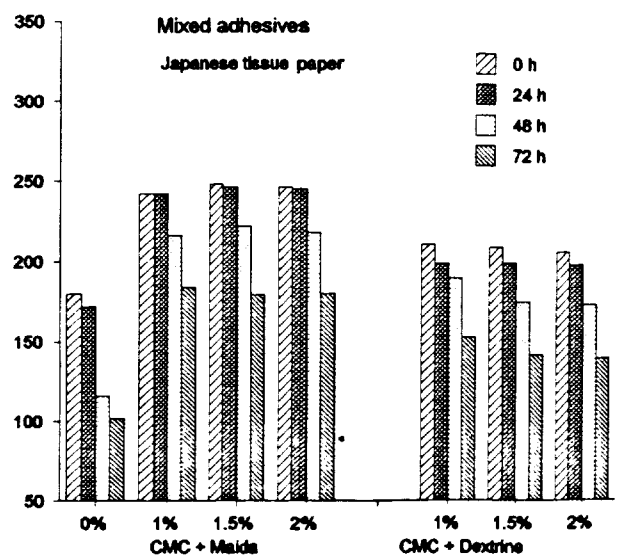

Fig. 4. Folding endurance before and after the accelerated ageing of Japanese tissue paper treated with mixed adhesives.

Results and Discussion

Our results show that all the adhesives had their individual characteristics despite having the same property of stickiness. Some of them showed good results on the supporting materials whereas others showed poor quality.

Carboxy methyl cellulose (CMC) and methyl cellulose (MC) were found to be quite similar in nature, both of them having a high degree of adhesive characteristic. The supporting materials applied with them showed high levels of strength and brightness. Even after accelerated ageing, the folding endurance was good, and the change in appearance was much less compared to the other adhesives. CMC and MC are easily soluble in water without heating, and a minimum quantity can be used to prepare satisfactory solutions for lamination. Their application to Nepalese handmade paper shows that even a 2.0% solution resulted in an increase of the original brightness from 55% to 68%, while the folding endurance capacity was very satisfactory even after 72 h of ageing.

Compared to the above chemicals, the maida (wheat flour) and dextrine

Table 3. Brightness of treated papers

Accelerated ageing		Nepalese handmade paper				Japanese tissue paper			
		0 h	24 h	48 h	72 h	0 h	24 h	48 h	72 h
	0%	55	55	54	51	94	94	93	93
Carboxy	1%	66	66	64	62	96	96	95	94
methyl	1.5%	68	62	60	57	96	95	95	92
cellulose	2%	68	60	60	55	97	96	95	92
Methyl	1%	67	67	62	61	97	98	96	85
cellulose	1.5%	67	67	60	61	97	96	95	82
	2%	68	65	60	59	97	97	95	82
Maida	1%	76	76	75	72	98	95	92	89
(wheat	1.5%	75	76	75	72	98	96	90	88
flour)	2%	76	75	74	72	97	96	92	88
Dextrine	1%	100	102	100	100	99	98	98	96
	1.5%	101	102	99	99	100	98	98	94
	2%	102	102	99	99	100	98	97	94
CMC	1%	76	76	75	71	87	87	86	83
and	1.5%	75	75	74	71	88	88	85	82
Maida	2%	76	75	74	69	89	88	86	82
CMC	1%	68	68	68	66	96	92	92	87
and	1.5%	68	69	68	67	97	92	92	87
Dextrine	2%	68	68	67	66	97	93	91	88

Table 4. Brightness of combined materials

Accelerated ageing		Chiffon+Nepalese paper				Chiffon+Japanese tissue paper			
		0 h	24 h	48 h	72 h	0 h	24 h	48 h	72 h
	0%	92	92	92	89	87	86	86	83
Carboxy	1%	78	78	77	74	89	89	88	87
methyl	1.5%	79	78	77	73	90	90	86	85
cellulose	2%	78	75	75	73	89	90	260	85
Methyl	1%	79	79	78	77	89	89	88	87
cellulose	1.5%	76	77	77	74	89	90	88	88
	2%	77	77	76	73	89	90	89	89
Maida	1%	79	79	79	73	89	90	89	84
(wheat	1.5%	79	79	76	74	90	90	88	83
flour)	2%	82	79	78	74	91	90	87	83
CMC	1%	78	78	76	72	88	88	84	81
and	1.5%	80	80	76	71	88	88	83	81
Maida	2%	77	76	74	72	89	88	84	80
CMC	1%	89	89	88	82	88	89	87	81
and	1.5%	88	90	86	81	89	89	86	80
Dextrine	2%	93	88	86	82	89	89	86	80

paste were found to be inferior in quality. Although the original brightness of the supporting materials was higher and the folds were acceptable on their application, their sticking property was not as good as that of the other adhesives. Compared with dextrine, maida paste had a reasonably good sticking property but only at 2% concentration. The dextrine had very little adhesive characteristic even at 2% concentration. Therefore a mixed study of CMC with maida and CMC with dextrine was carried out.

Tests of the brightness and folding endurance of the supporting materials did not show any appreciable difference in respect of the different concentrations of adhesive. However, some observations can be made.

- The brightness of the supporting materials increased with the application of adhesives.
- The brightness of the supporting materials coated with maida and dextrine was found to be of a comparatively higher level than in materials coated with other adhesives. This may be due to the high level of their original brightness.
- Compared to CMC and MC, the brightness results of maida paste and dextrine were found to be high; and their reduction caused by accelerated ageing

was found to be satisfactory. A serious drawback, however, was the poor sticking property of these compounds.

- In the mixed studies on CMC and maida paste and on CMC and dextrine, the brightness and folding results were found to be more reliable and the drop in percentage during accelerated ageing was also found to be smaller.
- The original brightness of Japanese tissue (94%) and chiffon (87%) was excellent and on application of adhesives it actually increased. Even after 72 hours of accelerated ageing, the colour did not change very much.
- With respect to the folding endurance of the supporting materials, in the case of Nepalese handmade paper coated with CMC and MC the folds were found to be satisfactory even after ageing for 72 hours. In the case of Japanese tissue the folds were observed to be less after ageing. Chiffon coated with many adhesives had the highest folding endurance. In this case the folds were measured up to 3000, and even after accelerated ageing the folds were not reduced below 2000. Only chiffon coated with CMC+dextrine provided a folding endurance below 2000 after accelerated ageing. The Indian tissue papers were found to have good folding endurance and a high level of brightness even after ageing.
- In all cases it can be observed that an increase in the concentration resulted in a decrease in the folding endurance as well in the brightness. The former may be due to increasing stiffness, and the latter to a higher opacity in the supporting materials.

Conclusion

Based on the results of the experiment, the following can be concluded.

- A thin adhesive application will always be more useful than a thicker one.
- Carboxy methyl cellulose and methyl cellulose can be used for lamination even in a concentration of 1%.
- Maida paste and dextrine in low concentrations do not have enough sticking ability, but mixing each with CMC or MC in 1:2 proportion results in a quality acceptable for application to supporting materials.
- As regards the supporting materials, all are useful, which means that they can be chosen according to the state of the object. If the document is very fragile and weak, a support of handmade paper or chiffon may be required. If, as in the case of laminating valuable records or documents, the application of a thick supporting material will result in reduced transparency, then tissue paper should be applied on the written face and a strong paper or chiffon should be applied on the unwritten reverse side of the object.
- Chiffon cloth in a yellowish or off-white colour is more useful than a white colour as support in documents.

Further studies will be undertaken in order to find out whether the Indian tissue paper procured from KVIC (Khadi and Village Industries Commission, Dehradun, India) can be a useful substitute for Japanese tissue paper.

Summaries

Evaluation of Adhesives and Supporting Materials for the Process of Lamination of Old Documents

A study of adhesives and supporting materials was carried out in order to develop methods of lamination for very old and weakened documents of paper and allied materials. This paper reports the use of simple and easily accessible materials and, on the basis of the study results, recommends adhesives and supporting materials that can be used effectively and successfully for the lamination.

Evaluation d'adhésifs et de matériaux de renfort pour la lamination de documents anciens

Une étude d'adhésifs et de matériaux de renfort a été réalisée afin de développer des méthodes de lamination de documents très anciens et affaiblis, en papier ou autres matériaux. Cet article propose l'utilisation de matériaux simples et facilement accessibles et, sur base des résultats de l'étude, recommande des adhésifs et des matériaux de renfort qui peuvent être utilisés avec efficacité et satisfaction pour la lamination.

Untersuchung von Klebemitteln und Stützmaterialien für die Festigung alter Dokumente

Es wurden Klebemittel und Stützmaterialien untersucht, um eine Methode zum Festigen von sehr alten und geschwächten Dokumenten aus Papier und verwandten Maerialien zu finden. Es wurden einfache und leicht zugängliche Materialien untersucht, und, basierend auf den Untersuchungeergebnissen, werden diejenigen Klebemittel und Stützmaterialien empfohlen, die effektiv und erfolgreich eingesetzt werden können.

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Hydroxypropyl Cellulose and Polyvinyl Alcohol on Paper as Fixatives for Pigments and Dyes

by MARINA BICCHIERI & BARBARA MUCCI

Introduction

The need to transmit our cultural heritage led humanity to the discovery of the art of writing, its media and supports; the further spread of culture in the world led to the invention of the art of printing.[1–4]

The most commonly used writing support is paper, and this can be degraded by hydrolytic or by oxidative mechanisms.

Hydrolysis occurs both in acid and in alkaline media,[5–10] the most important effect being a depolymerization of the cellulose chain. Alkaline hydrolysis takes place only at high temperatures and with strong alkalis, but if cellulose contains oxidized groups this plays a very important role. In this case alkaline hydrolysis occurs at lower temperatures, even with diluted alkalis, and it can become the chief degradative mechanism.

Almost all writing substances may damage the paper, either by producing an acid action (hydrolysis) or by inducing chemical deterioration (oxidation), due to the presence of metals, such as iron and copper.

Metallic cations in fact play a major role in cellulose degradation,[11–14] acting as a catalyst for the cleavage of the cellulose 1-4-β-glucosidic bond (Fe) or catalyzing the oxidation on the anhydroglucose ring (Cu).[15]

We can divide the writing media into two basic classes: *chemical inks*, which are chemically bonded with the cellulose fibres (oak gall inks, for example); and *pigment dyes*, which bond with the paper through an adhesive (gold or silver inks, cinnabar, lampblack, etc.). In the case of the pigment-based dyes, a degradation of the adhesive used for the ink can also take place.

The aim of our experiment was to find natural or synthetic adhesives for the restoration of graphic works of art, thus permitting the fixation of pigments without damaging the paper or changing the quality of the visual effect of all the colours. The fixing of the pigments, in fact, would mean that all restoring procedures, such as washing and deacidification could be applied.

We decided to investigate the possibility of employing of a hydroxypropyl cellulose (Klucel G) and a polyvinyl alcohol of low molecular weight (Unitika Poval UP-050), the former in an alcohol solution and the latter in a water-alcohol solution.

The polyvinyl alcohol (PVAl) we used has a hydrolysis degree of 87-89%; its average molecular weight is 14000. It is a white powder soluble in cold water and has an excellent resistance to ultraviolet radiation, to ageing and to biological agents.[16–21]

Until now, it has been applied in water solution. In our investigation we aimed at obtaining a water/ethanol solution, as many pigments are highly unstable owing to water action, and a mixed solvent should be less harmful.

The Klucel G (KG) is a hydroxypropyl cellulose of intermediate viscosity. It is soluble in many organic solvents and in cold water, but insoluble over 40°C.

Although this product is already used in restoration,[22–25] there are still some doubts[26] regarding its stability and interaction with the cellulose polymer chain.

We had two different aims in testing the two resins: the first goal was to check whether the Klucel G could change the chemical stability of the cellulose; the second goal was to verify the interactions between the two adhesives and the colours.

To analyse the chemical behaviour of the adhesives, we sprayed them on examples of white paper. After this treatment the samples were submitted to accelerated ageing along with examples of untreated paper for comparison.

To check the interactions between resins and colours, a preliminary investigation was carried out on their ability to fix and protect writing media. We then chose several different kinds of pigments and colours (wax-oil water-resistant pastels; soft pastels; water pastels; willow charcoal; and sanguine). Each pastel was applied on three sheets of paper. One sample was protected with Klucel G, one with Unitika-Poval UP-050, and one remained untreated for comparison. All samples were submitted to artificial ageing.

The ageing conditions, 80°C and 65% R.H., were chosen after submitting PVAl and KG to thermal analysis: at 80°C, in fact, there are neither transitions nor decomposition of either polymeric material.

Experimental Set-up

Materials

- Whatman paper no. 1 for chromatography
- Ethanol solution of Klucel G, 2% w/V

Hydroxypropyl Cellulose

- Ethanol/water solution of Unitika-Poval UP-050, 5% w/V (ratio H_2O/C_2H_5OH=4/6)
- Wax oil water resistant pastels (Caran d'Ache Neocolor I): black, yellow, red, green, blue, white
- Soft pastels (Rembrandt): black, yellow, red, green, blue, white
- Water pastels (Conté): black, yellow, red, green, blue, white
- Willow charcoal (Winsor and Newton)
- Sanguine (Koh-I-Noor)

Ageing

Untreated and treated samples were aged as follows:
- method ISO 5630/3-1981: 80°C 65% R.H.
- total time 28 days; drawing at 0, 7, 14, 21, 28 days

Measurements

On untreated and treated samples (without pastels), before and after each drawing time, measurements were made of:

1 pH of aqueous extract, hot extraction method (TAPPI T435 om-88)
2 Blue reflectance factor (ISO 2470/77)
3 Carboxyl content of cellulose (ASTM 1926-89)
4 Intrinsic viscosity of cellulose (modified ASTM 1795-90)

Measurements 3 and 4 were carried out only on untreated papers and on papers coated with Klucel G, the innocuity of polyvinyl alcohol on the cellulose polymer having already been demonstrated.[21]
All values of experimental data were corrected by the moisture content (ASTM D1348- 89). Measurements were executed on samples after conditioning at 23°C and 50% R.H (ASTM D685-87).

On all samples with graphic media, before and after each drawing time, measurements were made of:

5 chromaticity co-ordinates x, y, Y to quantify the colour differences before and after treatment with the adhesives and as a function of the ageing

Preparation of the Adhesives

a) Water-ethanol solution of polyvinyl alcohol 5% w/V
The polyvinyl alcohol was first dissolved in water (50 g PVAl in 300 ml of

water at 40–50°C, stirring and adding the powder slowly). After the complete dissolution of the polymer, the solution was diluted to ml 400 with water and then to ml 1000 with ethyl alcohol.

b) Ethanol solution of hydroxypropyl cellulose 2% w/V
20 g of hydroxypropyl cellulose were added slowly to 600 ml of ethyl alcohol during stirring.
After the polymer had swollen, forming a thick gel, 200 ml of ethyl alcohol were added and the solution was stirred for 30 minutes. The solution was left and after 24 hours it was diluted to 1 litre with ethyl alcohol.

Table 1. pH as a function of ageing time

Sample	Time: 0 days	7 days	14 days	21 days	28 days
Untreated (TQ)	6.60±0.02	6.40±0.02	6.16±0.02	6.04±0.02	6.03±0.02
Treated with Klucel G (KG)	6.63±0.02	6.40±0.02	6.24±0.02	6.12±0.02	6.80±0.02
Treated with Unitika Poval UP-050, (PVAl)	6.75±0.02	6.75±0.02	6.80±0.02	6.73±0.02	6.60±0.02

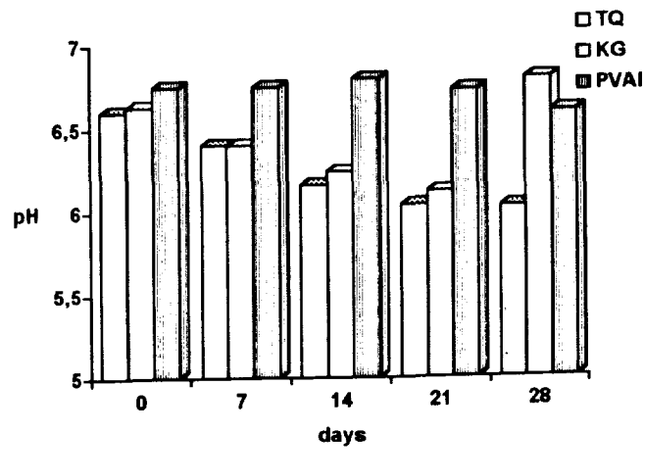

Fig. 1. pH as a function of ageing time and treatment.

Table 2. Diffuse blue reflectance factor (IRB%) as a function of ageing time

Sample	Time: 0 days	7 days	14 days	21 days	28 days
Untreated (TQ)	87.4±1.12	86.36±1.07	85.73±0.35	85.5±1.22	84.68±1.15
Treated with Klucel G (KG)	87.30±0.85	84.71±0.50	83.83±1.03	84.38±1.87	82.31±1.18
Treated with Unitika Poval UP-050 (PVAl)	87.50±0.10	84.30±0.50	82.40±0.30	82.00±1.10	81.70±0.40

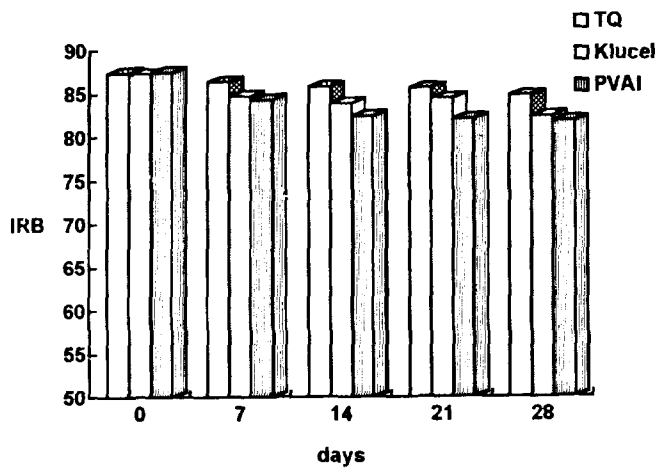

Fig. 2. Diffuse blue reflectance factor (IRB%) as a function of ageing time and treatment.

Results

pH

pH measurements were carried out in accordance with TAPPI T435 om-88, using freshly boiled, twice-distilled, carbon-dioxide-free water.

The results, listed in Table 1 and presented in Fig. 1, show that neither adhesive gave rise to an acidification of paper.

Brightness of paper

Diffuse blue reflectance factor (IRB%) measurements on untreated papers and papers protected with KG or PVAl are listed in Table 2 and presented in Fig. 2.

Carboxyl content

The carboxyl content of cellulose was analysed in accordance with ASTM 1926-89, by measuring the absorbance at 620 nm of a methylene blue solution. The analysis was based on the cationic exchange between COOH groups and methylene blue:

$$RCOOH+MB^{+} \leftrightarrow RCOOMB+H^{+}$$

(COOH=carboxyl groups in cellulose; MB^{+}=methylene blue)

which is proportional to the ratio $[MB^{+}]/[H^{+}]$.

A quantitative substitution of all carboxyl groups occurs in an alkaline buffered solution (pH 8–9).

The increase of oxidized groups in cellulose (COOH groups) causes a decrease

Table 3. Millimoles of carboxyl as a function of ageing time and treatment

Time (days)	Millimoles COOH±3% Untreated	Millimoles COOH±3% Klucel G
0	$4.89\cdot10^{-1}$	$4.30\cdot10^{-1}$
7	$4.96\cdot10^{-1}$	$3.93\cdot10^{-1}$
14	$4.91\cdot10^{-1}$	$3.76\cdot10^{-1}$
21	$4.90\cdot10^{-1}$	$3.83\cdot10^{-1}$
28	$4.55\cdot10^{-1}$	$3.99\cdot10^{-1}$

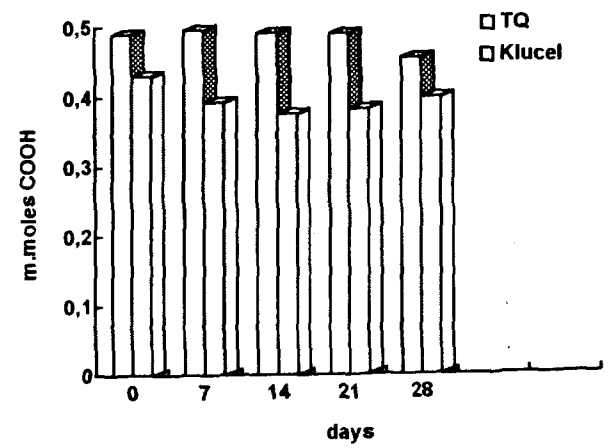

Fig. 3. Millimoles of carboxyl as a function of ageing time and treatment.

in methylene blue concentration, measured photometrically, which is a function of the ion-exchange capacity of cellulose. The results of the measurements, reported as millimoles of carboxyl per 100 g of cellulose, are listed in Table 3 and presented in Fig. 3.

Intrinsic viscosity

The behaviour Log $[(\eta_{rel}-1)/c]$ as a function of c was studied for each ageing time and treatment. η_{rel} is the relative viscosity of the solution of paper in cupriethylenediamine hydroxide (i.e. the ratio $\eta_{solution}/\eta_{solvent}$); c is the concentration of the cellulose solution in g/dl.

We decided to calculate $[\eta]$ by extrapolation at zero concentration, instead of obtaining the values of intrinsic viscosity $[\eta]$ from listed tables (ASTM or AFNOR methods).

The parameters of the straight line Log $[(\eta_{rel}-1)/c]$ vs c were obtained using a least-square-fit method, correctly taking into account, for each measurement, the proper error.

Table 4. $[\eta]$ as a function of ageing time

Sample	Time:	0 days	7 days	14 days	21 days	28 days
Untreated (TQ)		9.75±0.13	8.37±0.10	8.34±0.04	6.98±0.11	7.20±0.13
Treated with Klucel G (KG)		8.99±0.10	8.61±0.05	9.78±0.07	8.23±0.06	7.11±0.13

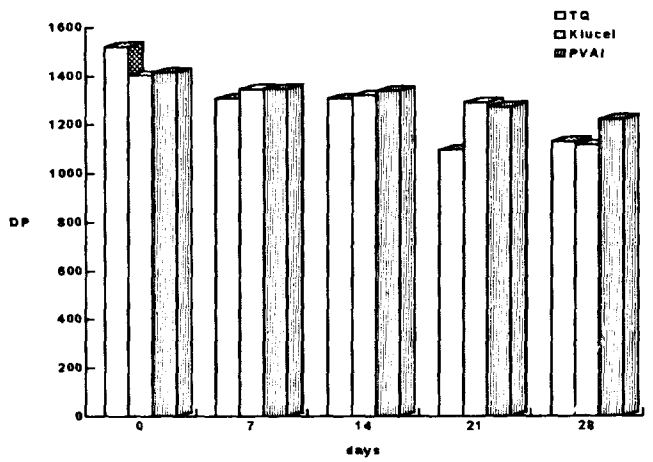

Fig. 4. Average degree of polymerization (DP^0) as a function of time.

Table 5. $[\eta_\infty]$ as a function of ageing time

Sample	Time:	0 days	7 days	14 days	21 days	28 days
Untreated (TQ)		8.56±0.08	8.25±0.06	7.99±0.05	7.60±0.05	7.07±0.06
Treated with Klucel G (KG)		9.04±0.05	8.71±0.07	8.48±0.06	9.84±0.13	8.23±0.04

The results are listed in Table 4 and presented in Fig. 4.

To evaluate the oxidation of the polymeric chain, we carried out other viscosity measurements after heating the solutions of paper in cupriethylenediamine hydroxide: the untreated samples and those treated with Klucel G were maintained at 60°C under nitrogen, for 1 hour.

These operating conditions can induce β-alkoxy-elimination mechanisms, which lead to the cleavage of the glucosidic bond in β to the group oxidized to aldehyde or ketone.

The average degree of polymerization (DP^∞) is lower than the corresponding DP^0 of the unheated samples: the higher the oxidation, the lower the DP^∞.

The measured "hot" viscosity $[\eta_\infty]$ values are listed in Table 5.

From Mark-Houwnik equations:

$$[\eta]=K\overline{M}_v^{\alpha}$$

$$[\eta]=K^1\,\overline{DP}_v^{\alpha}$$

we can calculate the average viscosity degree of polymerization, DP^0 from "cold" viscosity and DP^∞ from "hot" viscosity. These values are listed in Tables 6 and 7.

Fig. 4 reports the "cold" average viscosity degree of polymerization DP^0. The plotted values for PVAl were obtained in previous work.[21] Fig. 5 shows the behav-

Table 6. Average degree of polymerization (DP^0) as a function of time

Sample	Time:	0 days	7 days	14 days	21 days	28 days
Untreated (TQ)		1521±21	1305±16	1302±6	1090±17	1123±20
Treated withKlucel G (KG)		1402±15	1343±8	1315±11	1284±10	1109±20

Table 7. Average degree of polymerization (DP^∞) of heated samples as a function of time

Sample	Time:	0 days	7 days	14 days	21 days	28 days
Untreated (TQ)		1335±13	1287±10	1247±8	1186±9	1103±9
Treated with Klucel G (KG)		1411±8	1360±11	1322±12	1304±12	1285±7

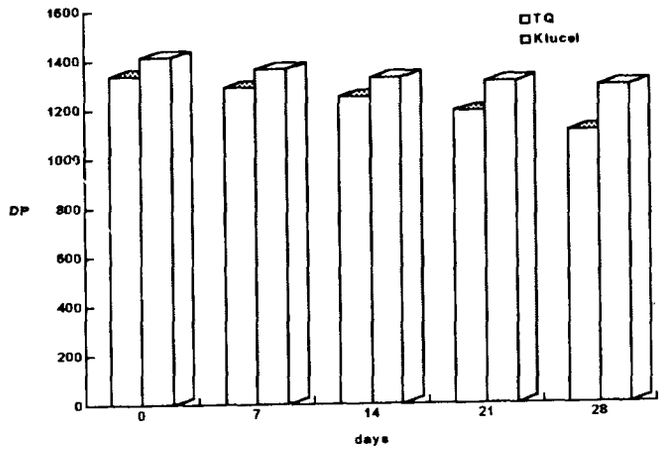

Fig. 5. Average degree of polymerization (DP_∞) as a function of time.

iour of the "hot" average viscosity degree of polymerization DP^∞ for the untreated papers and for the samples protected with KG.

Chromaticity co-ordinates x, y, Y

In 1777 George Palmer developed a theory, the essence of which was that all colours of light are composed of only three primary colours: red, blue and yellow. Further elaborations formed the basis of the trichromatic theory of colour vision.

The fundamental studies of Helmoltz, Grassmann and Maxwell led to the solution of the main problem for colour science, i.e. how to transform a subjective sensation of chromaticity into an objective series of numbers that could univocally define every tint.

It is now possible to choose several different methods to characterise a colour. We decided to use the Yyx chromaticity co-ordinates to test the sanguine, the charcoal and the remaining 17 different colours listed in the Experimental Set-up, i.e. various forms of black, yellow, red, green and blue. Each of these colours was also tested as 3 pastels: water-resistant pastels, soft pastels, and water pastels. In the white pastels (see Experimental Set-up) we measured the diffuse blue reflectance factor.

There was almost no variation in the XY chromaticity co-ordinates and only few variations in the Y co-ordinate (representing brightness), therefore only selected data are given in Table 8. Table 8 reports the values of the Y co-ordinates only for those colours showing an alteration of brightness during ageing. The blue reflectance factor of the white pigments is given in Table 9.

Table 8. Y co-ordinate (brightness) of selected colours as a function of ageing time

Colour	Sample	0 days	7 days	14 days	21 days	28 days
Yellow	untreated	96.37	60.47	61.13	57.98	57.84
soft pastel	treated with Klucel G (KG)	58.16	58.33	57.85	58.11	57.11
(Rembrandt)	treated with Unitika Poval UP-050 (PVAl)	51.77	52.42	52.98	51.71	50.60
Yellow	untreated	124.06	80.13	78.99	79.20	78.63
wax-oil pastel	treated with Klucel G (KG)	79.31	79.87	79.95	75.98	79.64
(Caran D'Ache)	treated with Unitika Poval UP-050 (PVAl)	78.74	77.39	77.39	76.90	77.43
Yellow	untreated	119.32	75.38	75.57	76.47	75.39
water pastel	treated with Klucel G (KG)	77.22	73.22	72.96	75.98	72.67
(Conté)	treated with Unitika Poval UP-050 (PVAl)	73.87	75.70	74.63	75.44	74.82
Green	untreated	15.62	15.24	15.07	15.63	14.70
soft pastel	treated with Klucel G (KG)	11.07	11.25	11.25	11.81	11.08
(Rembrandt)	treated with Unitika Poval UP-050 (PVAl)	7.10	6.80	7.12	7.01	6.77
Green	untreated	10.39	10.52	11.04	12.86	14.75
wax-oil pastel	treated with Klucel G (KG)	8.34	8.79	9.57	11.99	14.66
(Caran D'Ache)	treated with Unitika Poval UP-050 (PVAl)	7.18	7.14	8.56	11.80	13.23
Green	untreated	10.13	11.16	10.77	10.92	10.27
water pastel	treated with Klucel G (KG)	8.95	9.78	9.80	9.69	9.34
(Conté)	treated with Unitika Poval UP-050 (PVAl)	6.10	6.60	6.58	6.82	6.59
Black	untreated	2.72	2.01	2.03	2.00	1.95
soft pastel	treated with Klucel G (KG)	2.64	2.78	2.73	2.89	2.67
(Rembrandt)	treated with Unitika Poval UP-050 (PVAl)	3.17	3.05	3.27	3.34	3.04

DISCUSSION OF RESULTS

The experimental data show that neither KG nor PVAl cause acidification of the treated papers, the pH of which is stable during the whole ageing process and slightly less acid than the value for untreated papers.

In the ageing process, both polymers gave rise to a small diminution of the diffuse blue reflectance factor. This behaviour is, however, quite usual and always present if an adhesive is applied to the paper surface.

The analysis of the carboxyl content of the untreated papers and of those

Table 9. Diffuse blue reflectance factor (IRB%) of white pigment as a function of ageing time

Colour	Sample	0 days	7 days	14 days	21 days	28 days
White soft pastel (Rembrandt)	untreated	75.90	76.56	76.51	76.34	74.30
	treated with Klucel G (KG)	75.56	71.14	67.82	71.11	69.96
	treated with Unitika Poval UP-050 (PVAl)	65.94	61.88	65.17	62.12	54.25
White wax-oil (Caran D'Ache)	untreated	66.51	62.27	61.68	63.00	61.76
	treated with Klucel G (KG)	65.86	57.59	57.28	57.29	54.90
	treated with Unitika Poval UP-050 (PVAl)	67.23	59.71	60.38	57.75	58.82
White water pastel (Conté)	untreated	68.70	68.33	68.60	67.66	67.79
	treated with Klucel G (KG)	67.58	54.49	54.62	55.74	54.72
	treated with Unitika Poval UP-050 (PVAl)	64.50	52.92	56.44	55.86	47.86

treated with Klucel G is very interesting. The application of the artificial polymer in fact causes a diminution of the quantity of oxidized groups, and it seems to exert a protective action in relation to the cellulose chain.

This action, already shown for the PVAl, is more evident if we look at the average degrees of polymerization ("cold" and "hot"): after ageing the values for the treated papers are higher than for the untreated ones.

The most interesting data emerging from the measurement of chromaticity coordinates are those showing that the application of Klucel G or PVAl does not cause any variation in the chromaticity of the tested pigments. The only Y coordinate, representing brightness, shows a different behaviour pattern. Initially there was a variation in the brightness of almost all the pigments, but this difference decreased and finally disappeared during ageing in all the pigments, except for:

- green Rembrandt treated with PVAl, which showed a halving of the brightness;
- black Rembrandt treated with Klucel G or with PVAl, which showed an increase in brightness;
- green wax-oil colour and green water pastel treated with Klucel G or with PVAl, which showed an increase in brightness compared to the untreated sample; this increase was no longer evident after 21 days of ageing;
- white Rembrandt and white water pastel, the blue reflectance factors of which decreased after the treatment with both polymers, especially with PVAl.

We should like to stress that most of these changes (with the exception of green in linseed oil) were detected only instrumentally and not visually.

CONCLUSIONS

The main goal of this experimental work was to establish whether Klucel G could be applied in the conservative restoration of graphic works of art, without inducing chemical deterioration of the cellulose polymer chain and without changing the aesthetics of the pigments.

A further aim was to study the possible employment of a non-conventional water-ethanol solution of PVAl for the protection of pigments.[27]

All experimental data point to the fact that neither polymer is damaging to the cellulose and furthermore that they exert protection against chemical deterioration.

Optical measurements showed that Klucel G and PVAl did not signficantly alter the colours of the pigments to which they were applied. The measured changes of brightness, in fact, disappeared after a few days' ageing.

Other tests on the effectiveness of the fixing were carried out by immersing the protected pigments in water and in a deacidification solution. During and after the baths all pigments were stable and still remain so.

The ethanol solution of the adhesives also has a further use in the treatment of tracing paper, which cannot be restored by using water solutions.

SUMMARIES

Hydroxypropyl Cellulose and Polyvinyl Alcohol on Paper as Fixatives for Pigments and Dyes

The aim of this experiment was to find (semi-)synthetic adhesives for the restoration of graphic works of art, thus permitting the fixation of pigments without damaging the paper or changing the quality of the visual effect of all the colours. We decided to investigate the possibility of employing of a hydroxypropyl cellulose (Klucel G) and a polyvinyl alcohol of low molecular weight (Unitika Poval UP-050), the former in an alcohol solution and the latter in a water-alcohol solution. All experimental data point to the fact that neither polymer is damaging to the cellulose and furthermore that they exert protection against chemical deterioration. Optical measurements show that Klucel G and PVAl do not alter the colours of the pigments to which they are applied. Other tests on the effectiveness of the fixing were carried out by immersion of the protected pigments in water and in a deacidification solution. During and after the baths all pigments were stable and still remain so.

Hydroxypropylcellulose et Alcool de polyvinyle comme fixatifs de pigments et colorants sur papier

Le but de cette recherche était de trouver des adhésifs (semi)synthétiques pour la restauration d'oeuvres d'art graphiques permettant la fixation de pigments sans endommager le papier ou changer la qualité de l'effet visuel de toutes les couleurs. Nous avons décidé d'étudier la possibilité d'utiliser l'hydroxypropylcellulose (Klucel G) et un alcool de polyvinyle de faible poids moléculaire (Unitika Poval UP-050),

le premier en solution alcoolique et le second dans un mélange eau-alcool. Tous les résultats expérimentaux montrent qu'aucun des deux polymères n'endommage la cellulose et même qu'ils exercent une protection contre la détérioration chimique. Des mesures optiques montrent que la Klucel G et le PV alcool A1 n'altèrent pas les couleurs des pigments sur lesquels ils sont appliqués. D'autres tests sur l'efficacité de la fixation ont été réalisés par immersion des pigments protégés dans de l'eau et dans une solution de désacidification. Pendant et après les bains, les pigments sont stables et le restent.

Hydroxylpropylcellulose und Polyvinylkalkohol zur Festigung von Pigmenten und Farbstoffen auf Papier

Das Ziel der Experimente, über die hier berichtet wird, war es, (halb-)synthetische Klebemittel für die Papierrestaurierung zu finden, welche die Festigung von Pigmenten ermöglichen, ohne das Papier zu schädigen und ohne das Aussehen der Farben zu verändern. Wir entschieden uns zur näheren Untersuchung von Hydroxypropylcellulose (Klucel G) und niedermolekularem Polyvinylalkohol (Unitika Poval UP-050), ersteres in wäβriger und letzteres in Wasser-Alkohol-Lösung. Alle Meβdaten zeigen, daβ die beiden Polymere die Cellulose nicht schädigen, sondern im Gegenteil einen Schutz gegen chemischen Abbau bieten. Optische Messungen zeigen, daβ Klucel G und PVAl den Farbeindruck der Pigmente, auf die sie angewendet werden, nicht verändern. Weiter wurde das Verhalten der durch Klucel G und PVAl geschutzten Pigmente in wäβrigen Bädern und in Neutralisierungslösung untersucht: alle blieben während und nach einem solchen Bad stabil.

References

1. Bicchieri, M.: *La stampa ed i suoi inchiostri.* Storia e fondamenti della chimica, atti del V convegno nazionale. Roma: Acc. Naz. delle scienze, detta dei XL, 1993: 299–310.
2. Gallo, A.: *Liquidi scrittori.* Il libro. Roma: Tumminelli-Studium Urbis, 1946: 71–81.
3. Plossi Zappalà, M.: *Conservazione del manoscritto miniato: alchimia e preparazione dei pigmenti.* Arte documento 4 (1990): 268–275.
4. McLaren, K.: *A brief history of the development of colouring matters. The colour science of dyes and pigments.* Bristol: J. W. Arrowsmith Ltd, 1986: 1–11.
5. Mutton, D. B.: *Cellulose chemistry.* Pulp and Paper Mag. of Canada (1964): 41–54.
6. Blazej, A. & Kosik, M.: *Degradation reaction of cellulose and lignocellulose.* Cellulose and its derivatives. Chicester: Horwood, 1985: 97–117.
7. Whitmore, P. M. & Bogaard, J.: *Determination of the cellulose scission route in the hydrolytic and oxidative degradation of paper.* Restaurator 15 (1994): 26–45.
8. Feller, R. L., Lee, S. B. & Bogaard, J.: *The kinetics of cellulose deterioration.* In: Historic Textile and Paper materials. Edited by H. Needles & S. H. Zeronian. Advances in Chemistry Series 212 (1986): 329–347.
9. Atalla, R. H.: *Conformational effects in the hydrolysis of cellulose.* Advances in Chemistry Series 18 (1979): 55–69.
10. Santucci, L.: *Il ruolo della chimica nella conservazione del patrimonio librario.* Boll. ICPL 38 (1982-83): 121–148.
11. Shahani, C. J. & Hengemihle, F. H.: *The influence of copper and iron on the permanence of paper.* Historic Textile and Paper materials. Edited by H. Needles & S. H. Zeronian. Advances in Chemistry Series 212 (1986): 387–410.

12. Farrah, H. & Pickering, W. F.: *The effect of pH and ligands on the sorption of heavy metal ions by cellulose.* Aust. J. Chem. 31 (1978): 1501–1509.
13. Arthur, J. C. & Hinojosa, O.: *Oxidative reaction of cellulose initiated by free radicals.* J. Polymer Sci. 36 (1971): 53–71.
14. Sarybaeva, R. I., Sultankulova, A. S., Vasilikova, T. V. & Afanasiev, V. A.: *Degradation of cellulose in the presence of lewis acids.* Cell. Chem. Technol. 25 (1991): 199–210.
15. Bicchieri, M. & Pepa, S.: *The degradation of cellulose with ferric and cupric ions in a low-acid medium.* Restaurator 17 (1996): 165–183.
16. Santucci, L.: *Resistenza e stabilità della carta. III. Effetto dei collanti, con particolare riguardo a gelatina e alcool polivinilico.* Boll. ICPL 20 (1961): 145–157.
17. Plossi Zappalà, M.: *Indagine su adesivi per il restauro di documenti cartacei.* Boll. ICPL 34 (1976–77): 35–52.
18. Santucci, L. & Martinelli, G.: *Resistenza e stabilità della carta. IX. Collatura con gelatina, alcool polivinilico e ossietilcellulosa; venti anni dopo.* Boll. ICPL 37 (1981): 55–66.
19. Plossi Zappalà, M.: *Adesivi per il restauro librario e d'archivio. Effetto su carta.* Boll. ICPL 43 (1989): 79–96.
20. Gallo, F., Marconi, C. & Montanari, M.: *Ricerche sperimentali sulla resistenza agli agenti biologici di materiali impiegati nel restauro dei libri. VIII. Saggi sulla resistenza all'attacco microbico di adesivi.* Boll. ICPL 43 (1989): 105–120.
21. Bicchieri, M., Bortolani, M. & Veca, E.: *Characterization of low-molecular-weight polyvinyl alcohol for restoration purposes.* Restaurator 14 (1993): 11–29.
22. Hercules Inc.: Klucel: hydroxypropyl-cellulose.
23. Hofenk-De Graaff, J.: *Hydroxy propyl cellulose, a multipurpose conservation material,* Preprint ICOM Conservation Committee, 6th Triennial Meeting 19, 9 (1981): 1–7.
24. Bicchieri, M., Brusa, P. & Pasquariello, G.: *Tracing paper: methods of study and restoration.* Restaurator 14 (1993): 217–233.
25. Strnadova, J. & Durovic, M.: *The cellulose ethers in paper conservation.* Restaurator 15 (1994): 220–241.
26. Feller, R. L. & Wilt, M.: *Evaluation of cellulose ethers for conservation.* Marina del Rey, CA: The Getty Conservation Institute, 1990.
27. *Circolare Ufficio Centrale Beni Archivistici n°* 855/8.2.000, 21/3 (1991): In Italy, where this study was made, the use of PVAl has already been allowed in other restoration procedures by the Ministero per i Beni Culturali e Ambientali.

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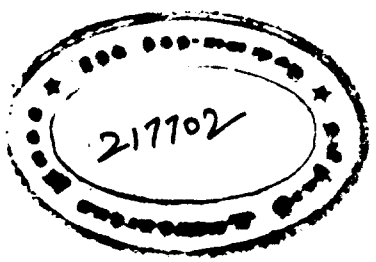

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