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The Bleaching of Paper by Reduction with the Borane Tert-Butylamine Complex

by MARINA BICCHIERI & PAOLA BRUSA

INTRODUCTION

The term "degradation" covers a series of cellulose reactions. From the chemical point of view, complete degradation leads to carbon dioxide and water. From the conservator's point of view, degradation occurs when a book or document or work of art loses some of its mechanical properties, such as mechanical strength.

Partial degradation can be so dangerous as to make the paper no longer usable.

Acids, strong alkalies and, under defined conditions, many oxidizing agents all cause partial degradation by different mechanisms but all leading to the loss of paper resistance[1–5].

Acids give rise to the hydrolysis of the cellulose, and thus the breaking of the glucosidic bond.

Strong alkalies are active only at a high temperature, causing alkaline hydrolysis. However, if cellulose contains oxidized groups the alkaline hydrolysis occurs at a lower temperature, even with diluted alkalies, and so plays a very important role.

The reactions of most oxidizing agents are unspecific and the study of oxycellulose is therefore very difficult. The result of the action of oxidants on the cellulose can lead to the breaking of the glucosid bond (as with acids and strong alkalies), or to the formation of carbonyl or carboxyl groups on the cellulose ring (anhydroglucose unit), or to the formation of double bonds C=C on the anhydroglucose unit.

Oxidative degradation takes place both in acid (for example periodic acid) and in alkali media (for example sodium hypochlorite).

The only primary hydroxyl group in the cellulose anhydroglucose unit generates an aldehyde group. The two secondary hydroxyl groups in the cellulose anhy-

Table 3. "Darwin!" by Ludwig Mingerade (Neue illustrierte Zeitung)

Measured point	Treatment	L*	a*	b*
1: Unprinted paper, bottom left	None	78.04	3.70	20.44
	Reduction	84.83	1.09	13.76
2: Brown colour, top right	None	32.85	5.18	7.79
	Reduction	34.68	4.82	6.50

Table 4. "Unter'm Weihnachtsbaum" by D.R. Wehle (Neue illustrierte Zeitung)

Measured point	Treatment	L*	a*	b*
1: Unprinted paper, bottom left	None	78.97	2.97	19.25
	Reduction	83.57	1.01	11.00
2: Child's dress	None	70.57	−0.04	13.87
	Reduction	72.32	−0.90	7.63
3: Grey colour on cat' s head	None	71.91	1.88	16.62
	Reduction	75.44	0.41	10.19
4: Dark colour behind child's head	None	37.62	4.53	9.37
	Reduction	41.09	3.43	8.68

Table 5. "Amor materno" by A. Ratti, and "Saffo" by F. Confalonieri

Measured point	Treatment	L*	a*	b*
1: Unprinted paper between the two prints, at the top	None	88.10	2.04	17.46
	Reduction	88.46	0.96	12.52

0.015 M (aqueous solution at pH=5 by hydrochloric acid) for a fixed time of 30 minutes.

The mechanism of the oxidation of cellulose by periodate leads to a formation of two aldehyde groups on C2 and C3.

Some of the oxycellulose obtained was left without reduction; the rest was then submitted to the action of the borane tert-butylamine complex for 1, 2, 3, 4 and 5 hours respectively.

We then calculated the average degree of polymerization of all the samples (oxidized and reduced after oxidation) from measurements of intrinsic viscosity of paper dissolved in cupriethylenediamine hydroxide.

The results of the measurements are reported in Table 7.

Table 6. "Ponte del Sestaione. Antica posta Oggi albergo dell'Abetone"

Measured point	Treatment	L*	a*	b*
1: Unprinted paper, bottom left "Antica posta"	None	69.88	−0.48	15.32
	Reduction	73.94	−1.49	11.35
2: Black colour, right arch "Ponte del Sestaione"	None	32.89	0.04	4.57
	Reduction	36.06	−0.07	3.93

Table 7. Average degree of polymerization of Whatman paper as a function of reduction time

Sample	Oxidation time	Reduction time	$\overline{DP}$
1	Untreated	Untreated	1521±20
2	30′		277±5
3	30′	1 h	1043±20
4	30′	2 h	1042±20
5	30′	3 h	1045±20
6	30′	4 h	1137±23
7	30′	5 h	1066±21

Table 8. Average degree of polymerization of ancient paper as a function of reduction time

Sample	Reduction time	$\overline{DP}$
A	Untreated	218±4
B	1 h	315±6
C	5 h	381±6
D	24 h	402±8

The ancient paper was submitted to reduction for 1, 5 and 24 hours. The results of the average degree of polymerization are reported in Table 8.

RESULTS

Chromaticity co-ordinates

Tables 1–6 report the chromaticity co-ordinates measured before and after the treatments at several coloured points on the printed papers. Fig. 1(a–b) shows the condition of print number 3 before and after reduction.

The explanation of colour co-ordinates is never easy. If two specimens have the same values of chromaticity co-ordinates, they are the same colour; conversely

droglucose unit can be oxidized to ketone groups and if a cleavage of C2 C3 bond occurs it is possible to obtain two aldehyde groups that can be further oxidized to carboxyl groups.

The normal deacidification treatments with calcium compounds are able to transform the acid carboxyl groups into stable insoluble salts, but they do not react with the other carbonyl groups (aldehyde or ketone). The presence of these functions in the cellulose polymer makes the acid and alkaline hydrolysis easier, and is in part responsible for the yellowing of the paper.

Much work has been undertaken[6 12] to discover a compound with selective reducing power for these groups. The borane tert-butylamine complex (also called tert-butylamine-borane; formula: $(CH_3)_3CNH_2 \cdot BH_3$) gave particularly good results in reducing aldehydes and ketones and it is also able to produce an optical bleaching of paper.

It is important to note that bleaching has so far usually been obtained with oxidant agents, which give reasonably white paper but which also induce oxidative and hydrolytic degradation mechanisms, thus weakening the paper strength.

Experimental Set-up and Measurements

In a previous study[13] we demonstrated the effectiveness of the borane tert-butylamine complex as a reducing and stabilising agent for the oxycellulose.

The aim of this new experiment is to test its application on several kinds of printed paper, with different graphic media and colours, as well as to optimise the time of application.

To test the behaviour of the reducing agent towards the colours, we worked on a privately-owned aquatint and on five prints that have not been catalogued and are only used for didactic purposes and research. These prints belong to the Istituto Nazionale per la Grafica.

1) Aquatint by R. Lorrain, 19th century
2) Coat-of-arms with two lions, 20th century
3) "Darwin!" by Ludwig Mingerade (Neue illustrierte Zeitung), 20th century
4) "Unter'm Weihnachtsbaum" by D.R. Wehle (Neue illustrierte Zeitung), 20th century
5) "Amor materno" by A. Ratti, and "Saffo" by F. Confalonieri, 20th century
6) "Ponte del Sestaione. Antica posta Oggi albergo dell'Abetone", 20th century

On the printed papers out, before and after the treatment, we carried out measurements of the chromatic co-ordinates [14] in the L*a*b* space. The obtained values are reported in Tables 1 to 6.

Table 1. Aquatint by R. Lorrain

Measured point	Treatment	L*	a*	b*
1: Light blue, sky, top left	None	54.78	1.21	13.87
	Reduction	68.44	−1.59	10.79
2: Light blue, sky between clouds, top left	None	55.40	2.51	15.00
	Reduction	68.73	−1.19	11.31
3: Cloud, top right	None	60.83	8.41	22.22
	Reduction	70.31	4.68	17.71
4: Yellow colour, in tree area, right	None	57.41	3.23	32.33
	Reduction	67.67	2.97	31.21
5: Yellow colour, under the tree	None	57.27	5.36	32.15
	Reduction	65.37	4.50	32.25
6: Brown colour of the house roof on the right	None	49.65	7.85	22.56
	Reduction	56.94	7.60	24.91
7: Dark brown colour, house roof on the right	None	40.15	4.91	15.57
	Reduction	41.12	5.09	15.85
8: Green colour, tree under house roof on right	None	36.88	−5.83	8.39
	Reduction	39.58	−6.43	8.77
9: Dark brown colour, bottom right	None	33.56	2.65	9.07
	Reduction	33.71	2.44	9.29
10: Red colour, roof on the right	None	40.15	11.46	16.79
	Reduction	52.48	11.82	23.87

Table 2. Coat-of-arms with two lions

Measured point	Treatment	L*	a*	b*
1: Yellow-gold colour, lion's paw	None	68.42	5.45	39.14
	Reduction	72.23	5.42	36.21
2: Red colour on the coat-of-arms, top left	None	51.95	24.17	19.11
	Reduction	53.32	25.87	18.56
3: Grey colour, top left	None	74.41	−2.16	10.82
	Reduction	77.47	−2.20	4.37

To optimise the application time of the reducing agent we used Whatman paper n° 1 for chromatography and an ancient original 19th century paper, without lignin.

Samples of Whatman paper were first oxidized with potassium periodate

Fig. 1. "Darwin!" by L. Mingerade: a) before reduction, b) after reduction.

if any co-ordinate value is different, the overall difference is a measure of the perceived colour difference between them.

One logical array of a selection of colours is based around a vertical axis (Fig. 2) with black at the bottom and white at the top (L* axis). Two other axes, a* and b*, represent respectively the green-red axis (from −a* to +a*) and the blue-yellow axis (from −b* to +b*). Each colour is a point in the three-dimensional space defined by L*a*b* co-ordinates. To put it simply: an increase of L* increases the luminosity of the colour; an increase of b* shifts the tint to yellow whereas its decrease means that the colour contains less yellow than before. The a* co-ordinate acts on the green-red axis: an increase of a* shifts to the red, and a decrease to the green. The most interesting co-ordinates in evaluating the effectiveness of the reducing treatment are L* and b*: in fact, if we remove a "yellowing" from a print we would expect to obtain an increase in luminosity (L*) and a decrease of the yellow content (b*).

In the examined prints we noted that the reducing treatment gave rise to an increase in the luminosity (L*) of all the colours. At the same time the b* co-ordinate decreased. The only exceptions were the yellow, brown and red-yellow colours in print 6. These colours already contained yellow before treatment. The reduction removed the patina with the result that the brighter colours became more intense and the b* co-ordinate thus increased. The a* co-ordinate always shifts to an intensification of the colour.

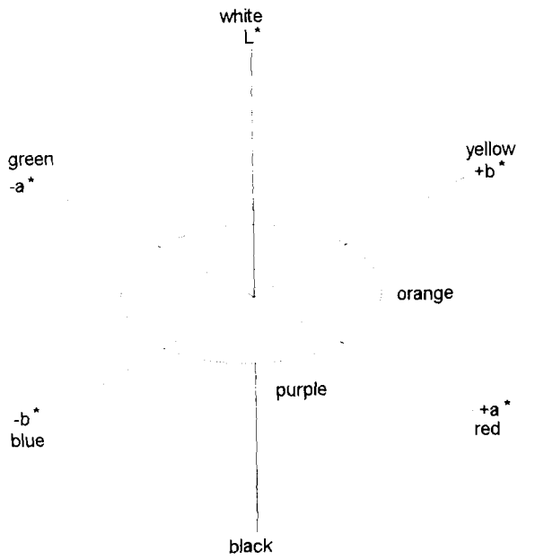

Fig. 2. L*a*b* co-ordinates.

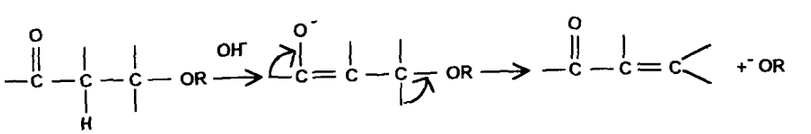

Fig. 3. β-alkoxy-elimination mechanism.

Viscosity measurements

The results of the average polymerization degree, from the viscosity measurements, are reported in Table 7.

We should like to stress that the low value of the polymerization degree of the oxidized unreduced cellulose (sample 1 in Table 7) is due to alkaline degradation in the cuprammonium solution and not to a chain scission during the periodate action. The periodate oxidation in fact gives rise to a formation of two aldehyde groups in the cellulose anhydroglucose ring. A β-alkoxy-elimination, the general scheme of which is given in Fig. 3, takes place in an alkaline medium and leads to cellulose chain depolymerization.

Table 9. Average degree of polymerization of unprinted paper of aquatint (print 1) as a function of reduction time

Sample	Reduction time	$\overline{DP}$
a	Untreated	171±5
b	2 days	259±8
c	5 days	381±10
d	7 days	386±10

This mechanism and the low value of the depolymerization degree obtained means that the oxidation has been effective.

Restoration of the aquatint

The print, showing a typical 19th century French village, is executed in aquatint on an extremely thick porous paper. The colours were severely yellowed and the edges without print had become brown due to the oxidation of the cellulose. There were also a large number of dark stains and raised incrustations.

The print had been attached with animal glue to a thick stiff card containing lignin, entirely unsuitable for conservation.

The first restoration task consisted in removing the card. This was gradually peeled off with the rapid application of compresses of tepid water, until the back of the print was reached.

The print was then washed in cold water to eliminate traces of adhesive and dirt. It was subsequently immersed for 48 hours, supported by non-woven tissue, in the borane tert-butylamine complex to reduce the oxidized cellulose. After removal from the reducing bath, the print was left to dry in the air at room temperature. The pre-existing tears were mended and the cuts sutured with methyl cellulose and Japanese paper of a suitable thickness.

The most noticeable result has certainly been the recovery of the intensity of the colours and the bleaching of the paper. The treatment brought the pH from 4.5 to 8.5 and also served to deacidify the work.

Conclusions

The effectiveness of the borane tert-butylamine complex has been demonstrated not only on artificially oxidized paper, but also on original prints. Moreover, the visual effect of all the prints is good. We have obtained greater contrast and the

colours have all intensified, losing their yellow patina but without changing their aspect.

As regards the optimisation of the application time, we can conclude that for the new artificially oxidized papers the degree of polymerization does not really change between 1 or 5 hours of immersion (see Table 7).

The ancient paper needed a longer treatment time, as shown in Table 8, probably because the reduction had also to act on double bonds C=C on the cellulose ring.

We chose a time of 5 hours for the prints as a compromise between the needs of the paper and the stability of the inks.

The time could be increased in the case of very oxidized papers. We obtained better results on small pieces of unprinted paper from the aquatint after 5 days' immersion in the reducing agent (see Table 9). The only consideration to be taken into account with such a long time concerns the stability and insolubility of the inks. For this reason the aquatint (the colour of which was very dark and brown) was treated for 2 days and not for 5 days.

We should like to underline the point that the reducing agent should not be used on modern stamping inks (i.e. those used to stamp papers) as these rapidly disappear when the treated with the borane tert-butylamine complex. This product should be used under a hood, with protective gloves, and away from open flame; it must also be disposed of as a toxic product – it must not be washed down the drain.

The EC risk classes are R 20/21/22 and R 36/37/38 (i.e.: harmful to inhale, ingest and have on the skin; and irritating to eyes, skin and respiratory system).

The EC safety classes are S26 and S37/39 (i.e.: in case of contact with eyes immediately rinse with plenty of water, get medical attention; avoid contact with skin and eyes, wear rubber gloves and goggles).

Summaries

The Bleaching of Paper by Reduction with the Borane Tert-Butylamine Complex

Acids, strong alkalies and many oxidizing agents cause degradation of cellulose, leading to the loss of paper resistance. The normal deacidification treatments with calcium compounds are able to transform the acid carboxyl groups into stable insoluble salts, but they do not react with the other carbonyl groups. The presence of these functions in the cellulose polymer makes the acid and alkaline hydrolysis easier and it is in part responsible for the yellowing of the paper. Much work has been undertaken to discover a compound with selective reducing power for these groups. The borane tert-butylamine complex gave particularly good results in reducing aldehydes and ketones and it is also able to produce an optical bleaching of paper. The aim of this experiment was to test its application on several kinds of printed paper with different graphic media and colours, as well as to optimise the time of application. The effectiveness of the borane tert-butylamine complex was demonstrated not only on artificially oxidized paper but also on original prints. The visual effect of all the prints was good. Concerning optimisation of the application time, we

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Conservation of Acid Paper:
Studies Carried out in the Chemistry Laboratory of the Istituto Centrale per la Patologia del Libro

by MARIAGRAZIA PLOSSI ZAPPALÀ

INTRODUCTION

The damage caused to paper by acidity has been known about for a long time. It is the most important cause of degradation, whether its origin is in ink, in the manufacturing processes (i.e. the residues of bleaching and resin and alum sizing), in external causes such as air pollution (sulphur or nitrogen oxides), or in handling and use. The β-glucosidic bonds of cellulose, while stable in a neutral or slightly alkaline environment, undergo hydrolysis in an acid environment, resulting in a considerable decrease in the pH of the paper, which in turn results in a fall in the degree of polymerization. Furthermore, it has been shown that the hemicelluloses are the more accessible as they are more amorphous than cellulose and hence more easily hydrolyzed by acids. In fact, the β-1,4 xylosidic and the β-1,4 mannosidic bonds of the hemicelluloses undergo acid hydrolysis even more rapidly than the β-1,4 glucosidic bond of cellulose. The oxidation of lignin, contained in paper produced with mechanical pulp, also contributes to the formation of acid compounds.

All these factors have brought about a considerably grave situation in the state of conservation of much of the world book heritage. Regarding the area concerning our Institute, i.e. Italy, there are millions of books in the libraries, most of which are printed and 70% of which date from the second half of the 19th century, the period rightly considered the watershed between paper manufactured with more permanent materials and that made with easily degradable components. Therefore the problem is quite pressing, particularly since no solution has yet been found for problems such as the conservation of paper containing mechanical pulp. The situation is also serious for paper manuscripts written with acidic ink based on metallic gallotannates, especially iron and copper. Although there are far fewer manuscripts than printed books, they nevertheless constitute an extremely precious part of our heritage. Holes in paper caused by acid ink are frequently found, as are larger losses of paper in the area of the written text, making consultation difficult, if not impossible.

PRELIMINARY RESEARCH

The urgency of dealing with these problems was recognized in the Chemical Laboratory of the Institute in the sixties when, throughout the world, different versions of the so-called "Barrow deacidification" procedure were being used. At that time we were already investigating the possibility of a connection between deacidification and sizing[1]. We noticed that in the experiments demonstrating the efficacy of the Barrow method, neither Barrow nor any other researchers had made any chemical measurements, apart from pH. Only mechanical resistance tests had been performed. Chemical measurements, however, such as the degree of polymerization, carboxyl and/or carbonyl content, alkaline reserve, etc. would have indicated even the slightest depolymerization of cellulose.

Furthermore, we noted that the concentrations of the saturated solutions of calcium and magnesium bicarbonates were not reproducible, resulting in a considerable variation in pH values. During these experiments we realized that the pH values must not be too high if paper shall have a good resistance to ageing. It must not be forgotten that, though it is risky to let a paper remain acid, it is also imperative to study the effect of alkaline solutions on non-acidic paper. Often, when acidity is due to the ink, the edge of the paper is not acidic, nor is it yellowed.

For these reasons we decided to deal with the problem systematically. Coordinated by L. Santucci, then director of the Institute's chemistry laboratory, we arrived at some particularly interesting conclusions. A solution of 0.002N of magnesium bicarbonate was suggested (150g of basic carbonate of Mg in 228 litres of water, with bubbling of CO_2 for 2 hours) at a concentration below saturation, thus facilitating preparation and reproducibility. This saved processing time, reduced the quantity of CO_2 used, and made it possible to recognize when transformation of carbonate into bicarbonate had occurred.

However, certain observations that emerged during this study meant that investigations had to be extended and, as a precautionary measure, the deacidifying solutions containing magnesium basic compounds being used at that time had to be abandoned. Compared to untreated cellulose, the cellulose in papers alkalinized with magnesium bicarbonate was significantly stabilized during accelerated "wet" artificial ageing (R.H. over 40%). Surprisingly, however, after "dry" accelerated artificial ageing at 105°C in a gravity convection oven, the degree of polymerization of the cellulose decreased. A less marked depolymerization was also

observed in the samples treated with calcium bicarbonate[2]. Although we were quite willing to believe that "wet" ageing answered our needs and was closer to natural ageing, and that Mg carbonates indeed had the protective effect observed during wet ageing, we wanted to understand why this phenomenon occurred.

Thus, the experiments were extended to alkaline solutions of a different nature and concentration, and to solvents other than water. We were already aware of the importance of finding a way to deacidify when inks and pigments were water-soluble. Thus saturated and unsaturated aqueous solutions of calcium bicarbonate, of magnesium bicarbonate (in a mixture or separately), of barium hydroxide, and alcohol solutions of magnesium acetate and barium hydroxide, were all tested. The technique of spraying with magnesium methoxide (the Smith method) was also tested, as was simple washing in running water.

ALKALINE SOLUTIONS OF METAL COMPOUNDS OF THE 2ND AND THE 1ST GROUP

The results of the studies of the effects of the alkaline solutions of calcium and magnesium carbonates and bicarbonates and of barium hydroxide were briefly presented at the I.I.C. Conference in Lisbon in 1972[3] [4] and in a more complete and detailed form at the *Colloque du CNRS* in Paris, again in 1972[5]. The results confirmed the following:

- The rate of deterioration of initially acid paper decreases after treatment with all the deacidifying solutions considered, whichever type of artificial ageing is used ("dry" or "wet");
- In the case of pure non-acid cellulose paper (Whatman), and particularly in the case of aqueous treatments, the result depends on the quantity of reagent absorbed and thus on the concentration of the solution. Furthermore, pure cellulose paper, rendered alkaline by treatments with aqueous solutions of carbonates and bicarbonates of the 2nd group metals, deteriorates more than untreated paper during "dry" ageing (and more markedly with magnesium compounds), while it deteriorates less than untreated paper when ageing is carried out in an environment with a relative humidity of 40% to 70% ("wet" ageing).

A number of degree theses investigating the problem of the effects of alkalinization of cellulose, were carried out for the Chemistry degree course at the "La Sapienza" University of Rome under the supervision of L. Santucci[6] [7] [8]. They dealt in greater detail with the behaviour of the alkaline solutions of salts and hydroxides of metals in the 2nd group in the Periodic System and, given the contradictory results, the question of which accelerated ageing method was the most

Table 1. Ionic contents of n°. 1 Whatman Chromatography Paper (millimoles/100g of paper[9])

K	Na	Ca	Mg	Fe	Cu
0,30	0,86	0,39	0,05	0,08	0,01

comparable to natural ageing arises. Investigations were also made into the behaviour of basic solutions of the carbonates and bicarbonates of the metals in the first group (sodium, lithium and potassium). Through Atomic Absorption Spectrophotometry it was determined that even the purest paper commercially available, i.e., Whatman for chromatography, contains traces of these metals.

A "deionized" paper was therefore prepared in the laboratory. Deionization was achieved by extracting the metal ions using a solution of HCl and HF 0.1N and then washing the paper in ultra-pure (twice-distilled) water until it was no longer acid (pH 7).

These experiments clarified the reason for the apparent destabilization of basic salts of magnesium during "dry" ageing. It was determined that sodium (in the form of carbonate) at extremely low concentrations (about 1 millimole per 100g of paper) during "wet" ageing is "beneficial" for conservation purposes, while at high concentrations it is definitely damaging. During "dry" ageing the beneficial effect occurs at higher concentrations. This led us to suspect that treatment with carbonates of Mg could remove traces of carbonate of Na, a residue of the manufacturing process, from non-deionized, pure cellulose paper. These hypotheses were confirmed during experiments, which also revealed certain important facts:

- Using Atomic Absorption Spectrophotometry on neutral pure cellulose paper (Whatman), far from negligible sodium contents were found: 0.86 mmoles per 100g of paper (Table 1). Treatment with solutions of magnesium bicarbonate eliminated some of the sodium contained in the paper. In fact, the sodium content in the paper decreased considerably after treatment (Table 2);
- In "wet" ageing, treatment with high concentrations of carbonates and bicarbonates of sodium caused severe degradation, while at very low concentrations it slowed down degradation. With "dry" ageing the positive effect also occurred at higher concentrations.
- On pure cellulose, deionized before treatment, the phenomenon connected with magnesium did not occur. Treatment with alkaline salts of Mg was always stabilizing, both with "dry" and "wet" ageing.

It was thus hypothesized that the difference in behaviour is linked to the fact that the solubility of the alkaline salts in the 1st group (e.g., sodium) is different to that of the 2nd group (e.g., calcium and magnesium):

The Bleaching of Paper

can conclude that ancient paper needs a long treatment time. We chose a time of 5 hours as a compromise between the needs of the paper and the stability of the inks. This time could be increased in the case of very oxidized paper, taking into account the stability and insolubility of the inks.

Le blanchiment du papier par réduction avec du tert-Butylamine borane

Les acides, les alcalis forts et beaucoup d'agents oxydants dégradent la cellulose entraînant une diminution de la résistance du papier. Les traitements de désacidification habituels avec des composés de calcium sont capables de transformer les groupes carboxyles acides en des sels stables insolubles mais ils ne réagissent pas avec les autres groupes carbonyles. La présence de ces fonctions dans le polymère celludosique rend les hydrolyses acide et alcaline plus faciles et est en partie responsable du jaunissement du papier. On a fait beaucoup de recherches pour trouver un composé avec une force réductrice sélective pour ces groups. Le tert-Butylamine borane a donné des résultats particulièrement bons en réduisant les aldéhydes et les cétones. Il est aussi capable de produire blanchiment optique du papier. Le but de ce travail expérimental était de tester son application sur différents types de papiers imprimés avec différents types de média graphiques et couleurs ainsi que d'optimaliser le temps d'application. L'efficacité du tert-Butylamine borane a été démontrée non seulement sur du papier artificiellement oxydé mais également sur des gravures originales. L'effet visuel sur toutes les gravures était bon. En ce qui concerne l'optimalisation du temps d'application, nous pouvons conclure que le papier ancien a nécessité un long temps de traitement. Nous avons choisi une durée de 5 heures comme compromis entre les besoins du papier et la stabilité des encres. Ce temps pourrait être augmenté en cas de papier très oxydé en tenant compte de la stabilité et de la solubilité des encres.

Das Bleichen von Papier durch Reduktion mit dem Tert-Butylamin-Komplex

Säuren, Alkalien und viele Oxidationsmittel bewirken den Abbau von Cellulose, was zu Festigkeitsverlust bei Papier führt. Die üblichen Neutralisierungsmethoden mit Calciumverbindungen können die sauren Carboxylgruppen in stabile, unlösliche Salze umwandeln, aber sie sind unwirksam in Bezug auf Carbonylgruppen. Das Vorhandensein solcher funktionaler Gruppen in der Cellulose erleichtert die saure und die alkalische Hydrolyse und ist einer der Verursacher von Vergilbung. Mit beträchtlichem Aufwand wurde nach Mitteln gesucht, die diese Gruppen gezielt reduzieren. Der Boran-Tert.Butylamin-Komplex zeigte besonders gute Ergebnisse beim Reduzieren von Aldehyden und Ketonen, und er bewirkt auch ein optisch wahrnehmbares Bleichen des Papiers. Das Ziel der Untersuchungen ist es, seine Anwendung auf verschiedene Arten von gedrucktem Papier bei verschiedenen Drucktechniken und Farben zu erproben und ebenso die optimale Anwendungsdauer zu ermitteln. Die Wirksamkeit des Boran-Tert-Butylamin- Komplexes wurde nicht nur an gezielt oxidiertem Papier gezeigt, sondern auch an originalen Drucken. Der optische Gesamteindruck aller Drucke ist gut. Was die optimale Anwendungszeit betrifft, so ist zu sagen, daß altes Papier eine längere Behandlungszeit erfordert. Wir wählten 5 Stunden als Kompromiß zwischen der erwünschten Wirkung auf das Papier und der Stabilität des Druckes. Bei stark oxidiertem Papier kann diese Zeit verlängert werden, wenn der Druck entsprechend stabil ist.

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Table 2. Ionic contents (in millimoles/100g of paper) of cellulose of deionized Whatman Chromatography Paper (1 Chr), treated with solutions of 0.005N sodium bicarbonate and then with solutions of 0.02N magnesium and calcium bicarbonate[9]

Type of treatment:	Ion: Na	Mg	Ca
Treatment 1: Deionized Whatman+ $NaHCO_3$ 0.005N	0,780	0,040	0,210
Treatment 2: Treatment 1 + $Mg(HCO_3)_2$ 0.02N	0,043	0,833	-
Treatment 3: Treatment 1 + $Ca(HCO_3)_2$ 0,02N	0,043	-	0,575

- Under "dry" ageing conditions the water content in pure cellulose paper treated with the alkaline solutions is minimal but sufficient to solubilize enough alkalis from traces of sodium salts normally contained in the paper due to the manufacturing process and therefore sufficient to exert a protective action, while the calcium and magnesium salts hardly dissolve in such a small quantity of water because of their low solubility and cannot provide sufficient alkali to exert a stabilizing action.
- The treatment of Whatman paper with solutions of basic salts of magnesium removes from the paper the traces of sodium carbonate which, during "dry" ageing, stabilizes the cellulose;
- In "wet" ageing, i.e., in the presence of a greater quantity of water, the concentration of alkali provided by the sodium deposit can be excessive, due to its higher solubility, and can cause degradation of the cellulose. This hypothesis was confirmed by a decrease in the degree of polymerization in the samples treated with alkaline salts of sodium during ageing, as well as a decrease in total alkalinity and in the pH (from pH 9 to about 7 and, in some cases, below 7). This can probably be explained by the production of acids.

These results were summarily presented at a seminar organized by the Società Chimica Italiana held in Perugia[10], and a more detailed report was presented at the Conference organized by the Institute of Paper Conservation at Oxford in 1986, and published in 1988[11].

NON-AQUEOUS DEACIDIFICATION

As mentioned above, the need for a deacidifying solution in a non-aqueous medium was pressing. Hence, in 1974[12] we published the results of a study on alcohol solutions of barium hydroxide, magnesium methoxide, and magnesium acetate:

- The magnesium methoxide spray (Smith-Wei T'o method) turned out to be a promising technique although, as with all the Mg compounds, it caused a superficial yellowing during "dry" ageing.
- Magnesium acetate did not give good results. The best solution tested was barium hydroxide in methanol 0.018 N (2.84g of Ba $(OH)_2$ $8H_2O$ per litre), a much more diluted concentration than that suggested by Baynes-Cope. It is nevertheless effective and does not leave the white deposits of barium carbonate resulting from the more concentrated solution. Unfortunately, this promising deacidifying method had to be abandoned because of the toxicity of the methanol and barium carbonate that remain on the sheets of paper after reaction between the hydroxide and the carbon dioxide of the air.

Another deacidifying technique was developed in 1981, with the collaboration of the I.C.P.L. Conservation and Restoration Laboratory[13] [14], using solutions of calcium acetate in water/methanol in varied proportions. This was a modification of the system previously suggested by M. Hey[15], which used the less toxic ethanol but was difficult to apply in some cases as hydroalcohol solutions of acetate of Ca with a low water content tend to form a *gel*. In the modified method, the document containing water-soluble pigments or inks was first tested with hydroalcohol mixtures (water/methanol) in various proportions, with the water content gradually increasing. The deacidifying solution of calcium acetate was prepared by dissolving the acetate in water and adding methanol until the proportions were equal to those of the hydroalcohol solution which, during the preliminary test, contained the highest water content possible without causing the pigments to solubilize. Unfortunately, despite all these expedients, treatment with hydroalcohol solutions of calcium acetate remained a rather weak method of deacidification.

In 1981 a further deacidifying treatment was developed[16] with Ca $(OH)_2$ in semisaturated aqueous solution, as previously suggested by M. Hey[17], and another in a solution diluted 10 times. This highly alkaline solution of calcium hydroxide acted as a fairly good deacidificant, which can simply be brushed carefully on to an acidic sheet. The system is particularly suited to deacidify a paper which has soluble pigments only on one side (water-colour prints, ink drawings, etc.). For these it can be used by simply placing the unpainted side of the paper on a filter paper soaked in the solution, or placing it, supported by a gauze of inert material, onto the surface of the solution (once called "water surface" treatment). In this way the sheet is slowly dampened from the *verso* and the operation can be controlled without damage to the soluble pigments. Very brief immersions of 1 or 2 minutes were also considered, to be used when pigments or inks are not easily soluble and can undergo such treatment without damage.

THE LATEST RESEARCH

In 1990 the initial results of a deacidification method using calcium propionate in an aqueous or alcohol solution[18] were presented at the 9th Triennial Meeting of the ICOM Committee for Conservation in Dresden. An aspect of this method that represents an innovation is the possibility of deacidifying at the same time as carrying out fungistat treatment. Propionate of Ca is a white powder which is highly soluble in water (40g in 100 cc at 0°C and 56g in 100 cc at 100°C) and slightly soluble in ethyl alcohol. An important characteristic is its non-toxicity. It is thus used as a preservative in food and in dermatological treatments. Its deacidifying power is good:

- A manuscript written in iron gallotannate ink with a pH of about 5 becomes pH 8.6 after treatment with an aqueous solution at 5% and after treatment with the saturated alcohol solution at pH 6.6.
- The pH of a printed book from 1929, acid and very yellowed, rose from 4.2 to 8.7 with the aqueous solution at 5%, and to 6.6 with the saturated alcohol solution, respectively.

The most surprising effect of propionate, which is positive for conservation, was seen on samples of Whatman paper previously oxidized with sodium hypochlorite at pH 7. We decided to test the effect of propionate on paper with this type of oxidation as it is particularly degrading for cellulose. In other words, we

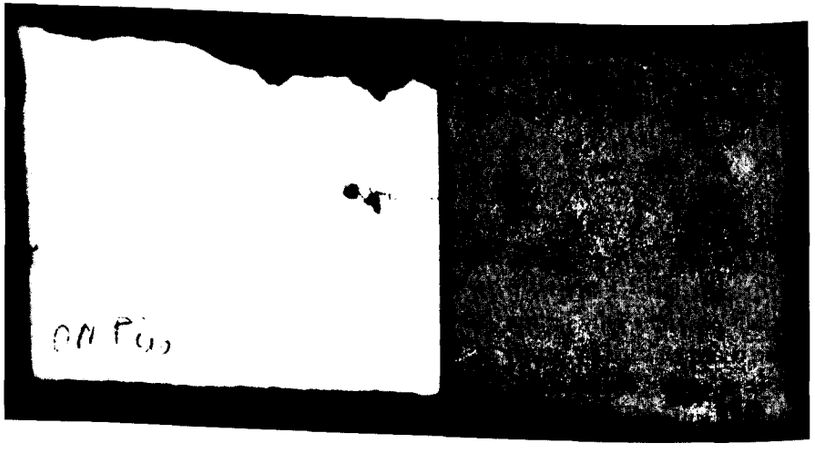

Fig. 1: Effect of calcium propionate on Whatman Paper previously oxidized with sodium hypochlorite at pH 7: after artificial ageing at 80°C and 65 % R.H. for ten days, the samples with propionate remained white whereas samples not treated with propionate became brown.

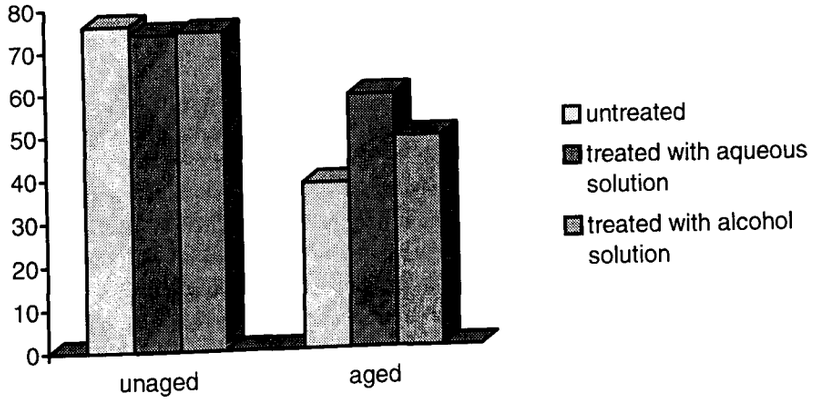

Fig. 2: Effect of calcium propionate on the brightness of Whatman Paper previously oxidized with sodium hypochlorite at pH 7. Ageing: 80°C and 65 % R.H. for ten days.

created the most drastic conditions possible. After artificial ageing, the samples oxidized with hypochlorite became considerably discoloured, while those oxidized and then treated with calcium propionate remained much lighter. Fig. 1 and 2 show the positive effect of the treatment on the degree of brightness. The definitive results of the research were published in 1994[19].

CONCLUSIONS

For some time, and especially after the latest research, the Institute's Chemistry Laboratory has come to the conclusion that, although acidity is undoubtedly the most serious threat to the conservation of the cultural heritage on paper, the alkalinization of paper must nevertheless be a controlled process. Not only must the pH not become too alkaline, but the "type" of alkalinity should be considered. The alkaline compounds of the metals in the 2nd group are preferable. Furthermore, it is not enough to consider only the effectiveness of a deacidifying treatment on acid paper, it is also necessary to assess the effect on neutral paper and on oxidized or pre-aged paper. While it is true that cleavage of the β-glucosidic bond is particularly accelerated in an acid environment and that this can occur in a basic environment only in particularly drastic conditions, it is nevertheless essential to remember that, if β-alcoxycarbonyl groups are formed because of oxidation, then degradation can take place rapidly even with diluted alkalis and at low temperatures (β-alcoxycarbonyl elimination)[9]. Thus, in recent years we have

turned our attention to the stabilization of oxidized paper through reduction treatments. Other researchers have already considered this problem and many have suggested sodiumborohydride as a stabilizer. However, this compound is very alkaline and, although it reduces the aldehydic and ketonic groups (as was observed through I.R. spectrophotometry), it can depolymerize the cellulose. In our laboratory we noticed that reducing previously oxidized papers with cyanoborohydride caused no damage of any kind and in general stabilized the cellulose. Yet, the method is particularly toxic and so cannot be used in normal conservation work. Original research, begun in 1990, for the first time experimented with the use of other boron compounds, i.e., the borane amine complexes. Among these, borane tert-butylamine complex seems to offer great possibilities for reduction and especially for safe bleaching. Some preliminary results were presented by P. Calvini and G. Martinelli at the Manchester Conference organized by the Institute of Paper Conservation in April 1992[20].

S. Pepa has recently concluded studies on these problems in a degree thesis in Chemistry at the "La Sapienza" University of Rome, under the supervision of M. Bicchieri[21]. S. Pepa has demonstrated that tert-butylamine borane induces an effective reduction of oxidized groups with a consequent slowing of the rate of degradation[22]. A practical application of reduction, accompanied by bleaching, was carried out with excellent results on various types of coloured prints, on ancient papers without lignin and on an aquatint[23].

SUMMARIES

Conservation of acid paper: Studies carried out in the chemistry laboratory of the Istituto Centrale per la Patologia del Libro

The paper reviews the main research work on deacidification carried out in the Chemistry Laboratory of the I.C.P.L. since the end of the 60s. Studies were made, in particular, on the effects of calcium and magnesium bicarbonates, of barium and calcium hydroxides and of magnesium methoxide. It is emphasized that treatment with deacidifying solutions, especially with calcium and magnesium bicarbonates, slows down the degradation of initially acid paper. The difference in behaviour of alkaline solutions of magnesium salts on non acid pure cellulose paper according to the type of artificial ageing is also noted: the influence on stability was negative during "dry" ageing (about 1–2% R.H.) and positive in "wet" ageing (R.H. > 40%). The effect is not noticeable on previously "deionized" pure cellulose paper. The subsequent studies showed that treatments with high concentrations of alkaline sodium salts are definitely damaging for conservation, while very low concentrations (1 mmole for 100g of paper) are "beneficial". It is thus hypothesized, in relation to accelerated artificial ageing, that the different behaviour of alkaline salts of the 1st group (e.g. sodium), compared to those of the 2nd group (e.g. calcium or magnesium), is linked to their different solubility.

Studies were also made on the effects of "non-aqueous" treatments with barium hydroxide and magnesium and calcium acetates in methyl alcohol. For aqueous deacidification of water sensitive pigments a "semi-saturated" aqueous solution of calcium hydroxide (diluted approximately ten times) was devised for use with short periods of immersion, or with particular expedients (using "water surface" treatment or soaked filter paper).

Finally, mention is made of the latest studies on deacidification with calcium propionate in aqueous or alcohol solution, a compound which unites deacidifying and fungistat properties and which turns out to be particularly effective on oxidized paper. The current research aimed at the *stabilization* of cellulose through reduction with borohydrides and with tert-butylamine borane complex is also discussed. It is concluded that:

- alkalinization of paper must be a controlled process: the pH must not be made excessively alkaline, and it must not be higher than 10;
- since the effect of alkalinization could be damaging to papers which are extremely oxidized but not acid (even though this is rare), it is also necessary to assess the effect of alkalinization on previously oxidized, or at least pre-aged, papers;
- the "type" of alkalinity to be given to the paper should also be considered: the alkaline compounds of metals in the 2nd group of the periodic table (calcium, magnesium) are preferable.

La Conservation du papier acide: Analyses du laboratoire de chimie de l'Istituto Centrale per la Patologia del Libro

On expose les travaux de recherche les plus importants qui ont été effectués depuis la fin des années 60 dans le domaine de la désacidification par le Laboratoire de Chimie de l'I.C.P.L.

Des analyses ont été faites pour étudier, en particulier, les effets des bicarbonates de calcium et de magnésium, ceux des hydroxydes de baryum et de calcium ainsi que ceux du méthylate de magnésium. On met l'accent sur le fait que le traitement avec des solutions désacidifiantes, comme en particulier avec des bicarbonates de calcium et de magnésium, ralentit la dégradation du papier initialement acide. On note également la différence de l'effet des solutions alcalines à base de sels de magnésium sur la stabilité du papier non acide en pure cellulose lors de différentes méthodes de vieillissement artificiel: l'influence est négative lorsque ça se passe „à sec" (1-2% humidité ambiante) et positive avec une méthode „humide" (h.a.> 40%). On ne constate aucun effet lorsque le papier en pure cellulose a été préalablement „désionisé".

Des analyses ultérieures ont permis de démontrer que les traitements utilisant de fortes concentrations de sels de sodium alcalins avaient un effet néfaste indéniable pour la conservation, alors que de très faibles concentrations (1 mole pour 100 g de papier) étaient „bénéfiques". A partir des deux effets exposés à propos du vieillissement artificiel accéléré on peut avancer l'hypothèse selon laquelle la cause de la différence de comportement des sels alcalins du 1er groupe (p. ex. le sodium) comparés à ceux du 2ème groupe (p.ex. le calcium ou le magnésium) réside dans la différence de leur solubilité.

On a aussi réalisé d'autres études pour analyser les effets de méthodes „non aqueuses", par exemple en utilisant de l'hydroxyde de baryum et des acétates de magnésium et de calcium dans de l'alcool méthylique. Pour réaliser une désacidification aqueuse des couches de couleurs sensibles à l'eau on recommande une solution aqueuse semi-saturée d'hydroxyde de calcium (diluée environ dans la proportion 1:10) à utiliser pendant de courtes périodes d'immersion ou à appliquer avec du papier filtre spécial imbibé de cette solution.

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Yellowing of Newspaper after Deacidification with Methyl Magnesium Carbonate

by VLADIMÍR BUKOVSKÝ

INTRODUCTION

Newspapers and magazines are usually printed on acid wood pulp paper – the cheapest, most widely available and therefore economically most appropriate material for a product of short-term use for a large number of readers. Such paper is not made for long-term storage in archives, much less for permanent display in a museum. Yet there are huge numbers of newspapers and other printed materials on wood pulp paper in libraries and archives. These can no longer be used because the paper has become brittle. Though they are mostly from the second half of the last century, the problem also extends to more modern materials. Their preservation has become a priority.

The process that can at least partly stop acid caused degradation of paper is deacidification, ideally combined with or followed by a subsequent strengthening. However, this process is not the absolute remedy, and when used for newsprint, can have negative side effects: In attempting to deacidify newspapers from the last century as well as modern ones with a non-aqueous solution of methyl magnesium carbonate dissolved in methanol[1], we encountered a significant yellowing of the paper. Brightness decrease must be considered a negative effect, and we therefore tried to assess the influence of light ageing on the yellowing of wood pulp paper. We did not study the influence of deacidification on acid degradation of cellulose and/or paper strength. Instead we concentrated on photooxidation and oxidation reactions in the lignin component, which have a decisive effect on the yellowing of paper.

YELLOWING

The most important factor in the yellowing of modern papers is the absorption of light radiation by certain chemical components of the polymeric structures of lig-

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Enfin on mentionne les dernières études faites sur la désacidification au moyen de propionate de calcium en solution aqueuse ou alcoolisée, c'est-à-dire sur une substance qui allie des propriétés désacidifiantes et fongicides et qui s'est avérée particulièrement efficace pour le papier oxydé. Les recherches poursuivies actuellement ont pour objectif la stabilisation de la cellulose par voie de réduction, que ce soit à l'aide d'hydrure de bore ou du complexe tertiaire de bore amino-butylique.

On conclut que:

- l'alcalisation du papier doit s'effectuer de façon contrôlée: le pH ne doit pas être trop alcalin ni excéder 10;
- étant donné que le traitement d'alcalisation peut avoir des effets néfastes sur les papiers qui sont extrêmement oxydés mais pas acides (même si ceci est rare), il faut analyser l'effet de l'alcalisation sur des papiers préalablement oxydés ou au moins sur des papiers préalablement vieillis;
- il faut aussi réfléchir au procédé de désacidification auquel on soumettra le papier: les sels alcalins du 2ème groupe du tableau périodique des éléments (calcium, magnésium) semblent préférables.

Die Konservierung von saurem Papier: Untersuchungen des Chemielabors des Istituto Centrale per la Patologia del Libro

Es wird über die wichtigsten Forschungen über Entsäuerung berichtet, die seit Ende der 60er Jahre im ICPL durchgeführt wurden. Insbesondere ging es um die Wirkung von Calcium- und Magnesiumbicarbonat, Barium- und Calciumhydroxid und Magnesiummethylat. Es wird betont, daß die Behandlung mit Neutralisierungslösungen, besonders Calcium- und Magnesiumbicarbonat, den Abbau von ursprünglich saurem Papier verlangsamt. Es wird auch hingewiesen auf die unterschiedliche Wirkung von alkalischen Lösungen von Magnesiumsalzen auf die Festigkeit von nicht saurem Papier aus reinem Zellstoff bei unterschiedlichen Methoden der beschleunigten Alterung: Sie ist negativ bei trockener (1–2% rF) und positiv bei feuchter (>40% rF) Alterung. Dieser Effekt tritt nicht auf, wenn der Zellstoff vor der Neutralisierung vollkommen gereinigt, d. h. frei von irgendwelchen Ionen gemacht worden ist. Weiter ergaben die Untersuchungen, daß Lösungen von alkalischen Natriumsalzen in hoher Konzentration einen deutlich negativen Effekt haben, während sie in niedriger (1 mmole/100 g Papier) positiv wirken. Man kann aus den beiden berichteten Effekten die Hypothese ableiten, daß die Ursache in der verschiedenen Löslichkeit von alkalischen Salze von Metallen der 1.Hauptgruppe des Periodischen Systems (z.B. Natrium) und derjenigen der 2. (z.B. Calcium oder Magnesium) liegt.

Es wurde auch die Wirkung von nichtwäßrigen Neutralisierungsmethoden untersucht, nämlich Bariumhydroxid, Magnesium- und Calciumacetat in Methanol. Zum Entsäuern von Blättern mit wasserempfindlichen Farbschichten wird ein kurzzeitiges Schwimmenlassen auf verdünnter Lösung von Calciumhydroxid (gesättigte Lösung: Wasser = 1 : 10) oder das Auflegen von Filterpapier empfohlen, das mit einer solchen Lösung getränkt ist.

Schließlich wird von den jüngsten Untersuchungen über Calciumpropionat in wäßriger oder in alkoholischer Lösung berichtet, d.h. über einen Stoff, der eine neutralisierende und zugleich eine fungistatische Wirkung hat und der sich als besonders wirksam bei oxidiertem Papier erwies. Die weiterführende Forschung gilt der Stabilisierung von Cellulose durch Reduktion, sei es mit Borhydriden oder mit dem Tert-Butylamin-Boran-Komplex.

Folgende Schlüsse werden gezogen:

- Das Entsäuern von Papier muß unter kontrollierten Bedingungen erfolgen: das pH darf nicht höher sein als 10.
- Da eine alkalische Behandlung für Papiere, die stark oxidiert, aber nicht sauer sind – was freilich nur selten vorkommt –, schädlich sein kann, ist es notwendig, die Wirkung einer Entsäuerung auf vorher oxidierte oder zumindest auf vorher gealterte Papiere zu untersuchen.
- Es muß auch die Art der Entsäuerung bedacht werden: die alkalischen Salze der 2. Hauptgruppe im Periodischen System der Elemente (Calcium, Magnesium) sind zu bevorzugen.

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nin, cellulose and other constituents of the paper (chromophoric groups During light absorption certain changes taking place in the chemical structures of the paper constituents gradually lead to the breakdown of chemical bonds. It is generally accepted that the yellowing reaction triggered by light absorption is an accompanying phenomenon of oxidation and that the process is initiated by free radicals produced by the absorption of light quanta.

Photooxidation is a complex combination of reactions in which, in addition to light, oxygen, atmospheric pollutants and impurities in the paper are involved. Yellowing observed after long-term storage of materials is to a large extent caused by temperature and moisture[2].

The main constituent of paper – cellulose – absorbs light mainly in the UV region, i.e., below 200 nm, and is considered a bad absorber of visible light. The presence of oxygen causes the formation of hydroperoxides[3] that are changed by light into radicals that form light sensitive carbonyl and carboxyl groups. The sensitivity of cellulose to colour change depends on the number of these groups in its macromolecule. Photooxidation results in yellowing and even browning of paper. Diffused light or light lacking the UV component, however, has little influence on these reactions[4]. Hemicelluloses behave similarly to cellulose.

The lignin content in paper varies and depends on the papermaking process and the quality (brightness) requirements for the produced paper. Lignin is the second largest constituent of wood pulp paper. It differs greatly from cellulose in its chemical structure[5]. It shows strong light absorption in the UV range with a distinct peak at 280 nm, gradually decreasing after 350 nm in the visible part of the spectrum. The photooxidation reactions are considered the major factors in the degradation of lignin[6,2].

Table 1: Grammage and alkaline reserve

Paper no.	g/m² C	standard deviation (4 samples)	g/m² M	standard deviation (4 samples)	g/m² MMC	standard deviation (4 samples)	% increase (MMC/M *100–100)
1	86,20	2,33	86,33	2,66	91,66	1,93	6,17
2	61,42	1,34	65,16	0,41	67,67	1,96	3,85
3	61,82	1,16	60,33	1,21	64,83	1,35	7,46
4	58,44	1,07	58,67	1,89	64,42	0,74	9,80
5	54,66	1,76	54,10	2,33	56,00	1,14	3,51
6	54,17	1,35	57,11	1,08	61,11	1,41	7,00
7	46,83	1,33	49,16	1,42	51,67	1,35	5,11

Among the different groups in the structure of lignin (primary, secondary, phenolic hydroxy, carbonyl, carboxyl, ether linkages), phenolic hydroxy groups are the most sensitive to photooxidation. In the presence of oxygen in the air they easily oxidize to coloured (yellow) semiquinonoid and quinonoid structures. The formation of phenoxy radicals from free phenolic OH-groups is an important factor in yellowing when light is present, while carbonyl groups of phenylpropanoid structures of lignin that operate as photosensitizers are decisive. The intensity of paper yellowing is proportional to the amount of the latter[4,2]. To prevent yellowing or to partially remove existing colouration of wood pulp papers, the number of carbonyl groups must be reduced or the free phenolic OH-groups must be blocked by esterification or etherification. Yellowing is greatly reduced by the presence of antioxidants in paper[4].

EXPERIMENT

Paper samples

As sample papers for our research we used the following:

- no. 1: Whatman chromatographic paper No. 1 (W1)
- no. 2: regular wood-free writing paper
- no. 3: the Slovenka journal paper
- no. 4: the Cas newspaper
- no. 5: the Práca newspaper
- no. 6: the Zivot Turca newspaper
- no. 7: the Pesti Hirlap newspaper form the year 1936

Treatment

Each of the paper samples was divided into three groups: The first was the untreated paper (C) the second, the paper extracted in pure methanol (M) (since paper degradation products are partly washed out by methanol); and the third, the paper deacidified in a 5% methyl magnesium carbonate solution in methanol (MMC)[1].

All samples were conditioned at 60% RH, 21°C, the M and MMC samples after evaporation of the methanol. The alkaline reserve $MgCO_3$ was assessed as a weight difference between M samples (washed in methanol) and the MMC samples. The results are given in Table 1.

Table 2: Brightness of the papers before and after deacidification with MMC

Paper no.	brightness C	standard deviation (6 samples)	brightness M	standard deviation (6 samples)	brightness MMC	standard deviation (6 samples)	% change (MMC/M *100-100)
1	100,00		99,75	1,39	99,01	1,77	-0,74
2	93,50	0,76	93,25	0,88	91,75	1,11	-1,61
3	78,62	0,74	77,37	1,06	74,75	1,39	-3,39
4	82,83	1,17	82,12	1,92	74,25	1,48	-9,58
5	69,30	1,58	69,25	0,71	58,87	1,13	-14,99
6	66,12	1,25	65,17	0,75	59,50	1,51	-8,70
7	59,12	1,01	61,13	0,33	54,25	1,03	-11,25

Exposure of samples

The process of light ageing of the newspaper sheets was divided into two stages. In the first, the paper was exposed to indirect daylight behind window glass for 185 days in the winter (September through beginning of March). The brightness was measured on the day of deacidification and then after 1, 16, 55, 79, 134, and 185 days of exposure. The data from days 1 and 185 are given in Tables 2 and 3, those of all are represented in Fig. 1. The brightness of the reverse side was measured after 2 and 55 days of light ageing. The next experiment was to place the paper samples in regular storage conditions, i.e., 50-55% RH, temperature 20±2°C, with no light access, for a 5½ year period. Brightness of the exposed and reverse sides is given in Tables 4 and 5.

Table 3: Brightness of the papers after 185 days exposure to daylight

Paper no.	brightness C	brightness M	brightness MMC	% change (MMC/M *100-100)	% change (M_{185}/M_1 *100-100)	% change (MMC_{185}/MMC_1 *100-100)
1	98,60	98,52	95,63	-2,93	-1,23	-3,41
2	90,51	90,77	89,33	-1,59	-2,66	-2,64
3	65,63	61,50	64,80	5,37	-20,51	-13,31
4	68,72	70,32	67,33	-4,25	-14,37	-9,32
5	55,30	55,83	52,23	-6,45	-19,38	-11,28
6	53,38	53,85	52,23	-3,01	-17,37	-12,22
7	55,13	54,90	51,55	-6,10	-10,19	-4,98

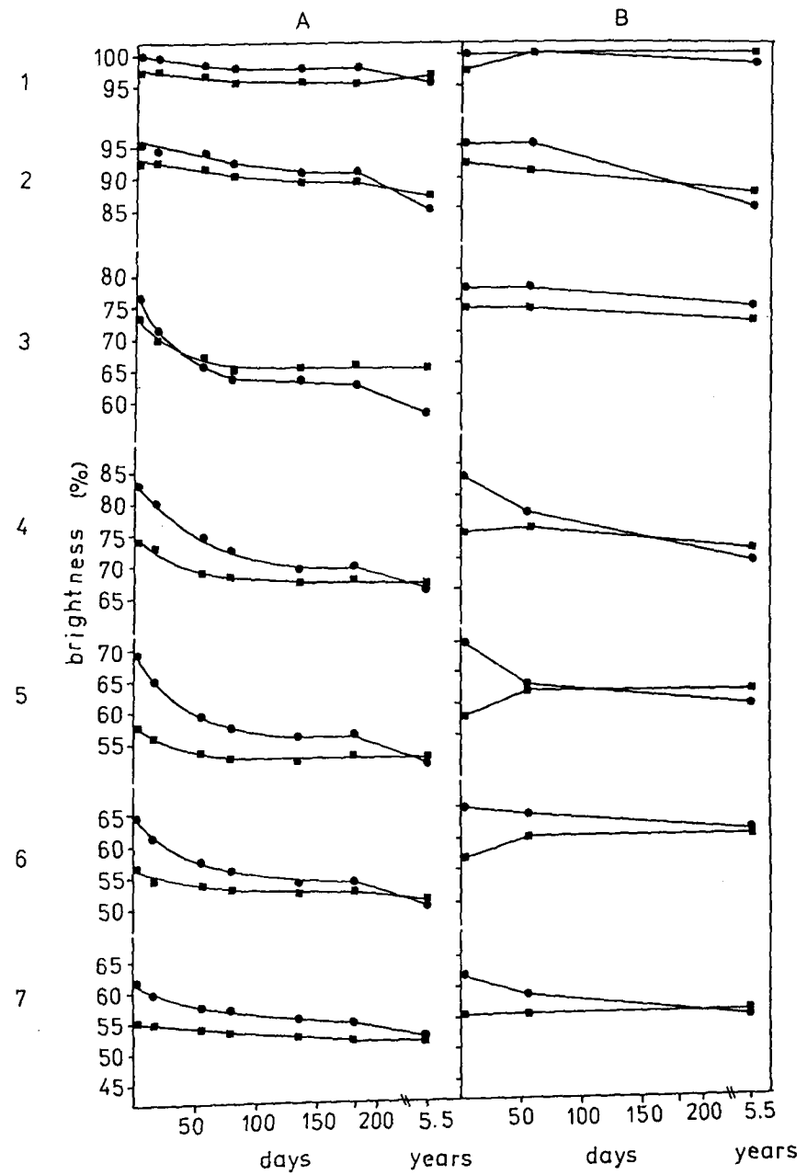

Fig.1. Brightness of the papers on the exposed (A) and the reverse side (B) in the course of 185 days and after 5½ years of storage. Round point: washed in methanol (M); square point: deacidified (MMC)

Table 4: Brightness of the exposed side of paper after 185 days exposure to daylight followed by 5½ years storage

Paper no.	brightness C	standard deviation (4 samples)	brightness M	standard deviation (4 samples)	brightness MMC	standard deviation (4 samples)	% change (MMC/M *100-100)
1	94,10	0,89	95,91	1,01	96,73	0,95	0,86
2	85,90	0,72	84,82	0,44	87,10	0,87	2,69
3	61,18	1,00	57,01	1,15	63,83	1,07	11,96
4	64,43	0,98	65,67	0,91	66,05	1,28	0,58
5	52,33	0,59	51,13	0,75	51,63	0,67	0,98
6	49,73	0,81	49,87	1,17	50,47	0,35	1,20
7	52,28	0,59	52,27	0,50	51,85	1,52	-0,80

Measuring of brightness

The paper samples were measured for brightness with a Spekole Zeiss (Germany) in the modified turbidimetric unit adjust with a wavelength of 412 nm[7]. The wavelength was assessed from the spectral reflectance curve of the paper colour after deacidification with MMC. Whatman No. 1 was used as a reference for 100% brightness paper. Brightness was measured on the light exposed side of the paper samples as well as on the protected, reverse side.

Table 5: Brightness of the reverse side of paper after 185 days exposure to daylight followed by 5½ years storage

Paper no.	brightness C	brightness M	brightness MMC	% change (MMC/M *100-100)	% change (M_{rev}/M_{exp} *100-100)	% change (MMC_{rev}/MMC_{exp}
1	98,51	98,29	100,00	1,74	2,48	3,38
2	86,53	87,81	86,30	-1,72	3,53	-0,92
3	66,07	72,63	70,37	-3,11	27,40	10,25
4	69,50	68,67	70,20	2,23	4,57	6,28
5	58,83	58,93	61,22	3,89	15,26	18,57
6	60,47	60,00	60,23	0,38	20,31	19,34
7	57,25	55,37	55,97	1,08	5,93	7,95

Table 6: Brightness of the papers after the reaction with sulphanilic acid

Paper no.	brightness C	standard deviation (4 samples)	brightness M	standard deviation (4 samples)	brightness MMC	standard deviation (4 samples)	% change (MMC/M *100-100)
1	98,25	1,36	99,01	1,12	99,26	0,95	0,25
2	94,00	1,15	91,50	1,91	91,24	2,21	-0,28
3	62,52	0,58	60,10	0,82	74,25	0,95	23,54
4	63,33	1,52	64,02	1,48	73,53	1,00	14,85
5	50,54	1,15	51,03	1,82	57,75	0,96	13,17
6	47,75	0,53	47,66	1,15	57,10	1,01	19,81
7	49,11	1,16	48,25	0,53	53,81	0,96	11,52

Reaction with sulphanilic acid

To determine the reason for the colouration of wood pulp papers after deacidification with methyl magnesium carbonate, the samples from Table 2 (C, M and MMC, not exposed to light) were dipped into sulphanilic acid solution used as a colour indicator for lignin (wood pulp) in paper[7]. The results are given in Table 6. Brightness reversion was repeatedly measured at a wavelength of 412 nm. We found that the C and M samples linked sulphanilic acid much more dramatically than the MMC samples, i.e., the deacidified papers. This suggested that during deacidification a chemical reaction of methyl magnesium carbonate with phenolic groups of lignin took place in alkaline environment resulting in magnesium phenolates. Magnesium linkage with lignin may be of a lignin-O-Mg-O-lignin type or a lignin-O-Mg-O-CH_3 type. On the one hand this linkage causes yellowing of paper, but on the other hand it prevents the change of the sulphanilic acid linkage to a phenolic OH group. The latter caused a significant decrease in brightness in the C and M samples, in nearly the same values after deacidification. The change in brightness caused by the deacidification treatment was thus quite high. The increase was between 11.5 and 23.5%, while without the lignin indicator there was a decrease of between 3.4 and 15% (cf. Tables 6 and 2).

Carbonyl groups and lignin

After both the period of exposure to daylight for 185 days and of storage for 5½ years we measured the carbonyl groups content (according to the Albertsson and Samuelson photocolorimetric hydrazine method[10]) as an indicator of degree of oxidation[8,9]. We also measured the lignin content of the papers (according to the

König and Rump method[11]). After dissolving the cellulose in 72% sulphuric acid, a brown, insoluble lignin was left (so-called Klason's lignin). Its content was expressed as a percentage of the dry weight of the paper. The amounts of both carbonyl groups and lignin are given in Table 7.

Table 7: Carbonyl and lignin contents after 185 days exposure to daylight and 5½ years storage

Paper no.	carbonyls (mmol/100g) M	std. dev. (3 s.)	carbonyls (mmol/100g) MMC	std. dev. (3 s.)	% change (MMC/M *100–100)	lignin (g/100g) M	carb./ lign. (mmol/g) M	MMC
1	0,47	0,09	0,23	0,03	-51,06	0	0	0
2	2,59	1,34	1,57	0,41	-39,38	0	0	0
3	15,78	1,91	9,38	0,72	-40,56	10,0	1,58	0,94
4	11,64	0,54	6,83	0,14	-41,32	13,4	0,87	0,51
5	26,20	1,18	15,78	0,47	-39,77	16,1	1,63	0,98
6	21,70	1,58	11,15	0,57	-48,62	14,1	1,54	0,79
7	28,67	0,97	19,86	0,60	-30,73	22,3	1,29	0,89

Electron microscopy

After 185 days of light ageing, samples of M and MMC were submitted to electron microscopy scanning (Tesla BS 340, Czech Rep.) to assess possible structural changes on the exposed side. Fig. 2 shows the surface of papers 1, 6 and 7 after bathing in methanol (M) and after deacidification (MMC). The structures of various fibres are visible, as well as various degrees of paper sizing, but no changes caused by deacidification.

Results and Discussion

While normally the grammage of newsprint is 54–58 g/m², the grammage of the papers tested for our project was between 47 and 86 g/m², the lowest belonging to the newspaper from 1936 (paper 7). The brightness of the modern papers was between 66–83% of that of the reference sample (Whatman chromatographic paper No. 1). The historic newspaper had only 59% of the brightness of the reference sample (Table 2). The old paper (sample 7) demonstrated that a bath in methanol can extract some degradation products, so that brightness is marginally increased.

Deacidification of newsprint resulted in yellowing in all cases (Table 2). The degree was between 3.4% and 15%, and corresponded to the lignin content in the

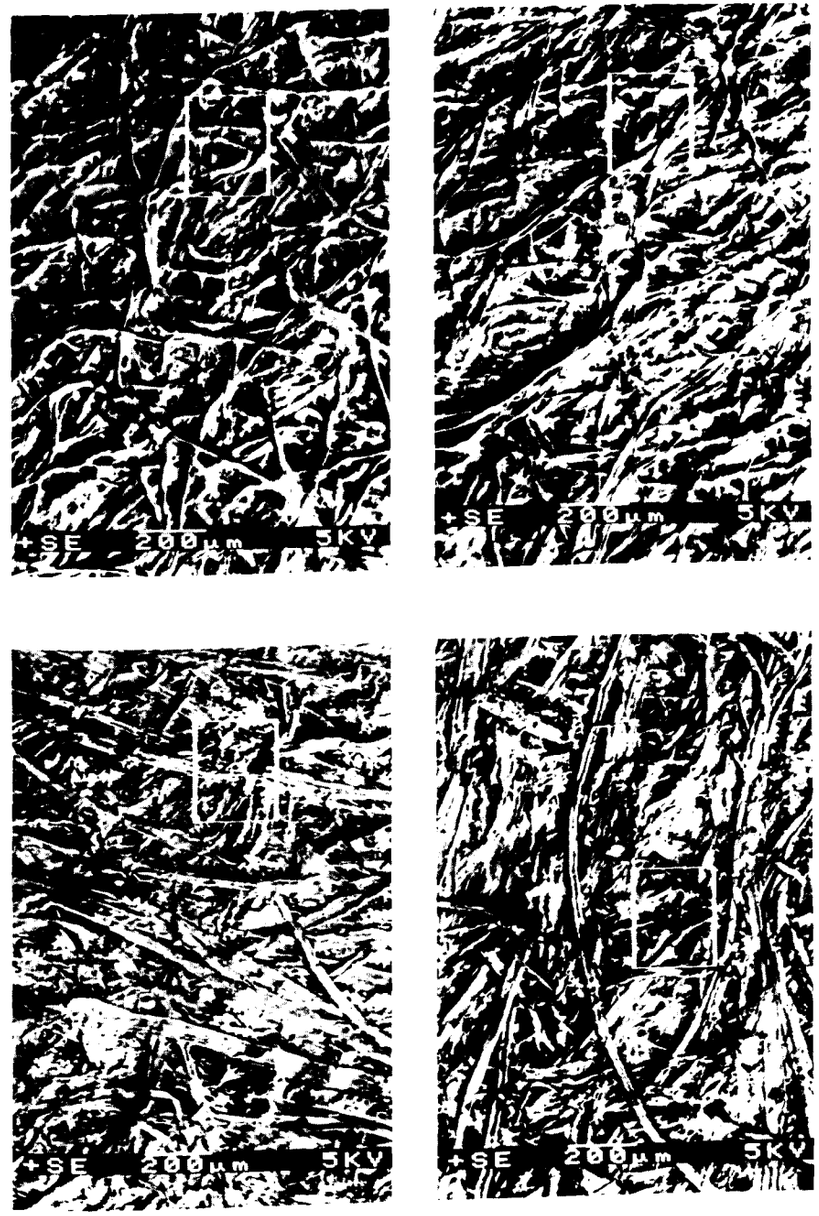

Fig. 2 a: The surface of paper 1 and 6 after 185 days exposure to UV-reduced daylight. Magnification factor: 100. Left: washed in methanol (M); right: deacidified (MMC).

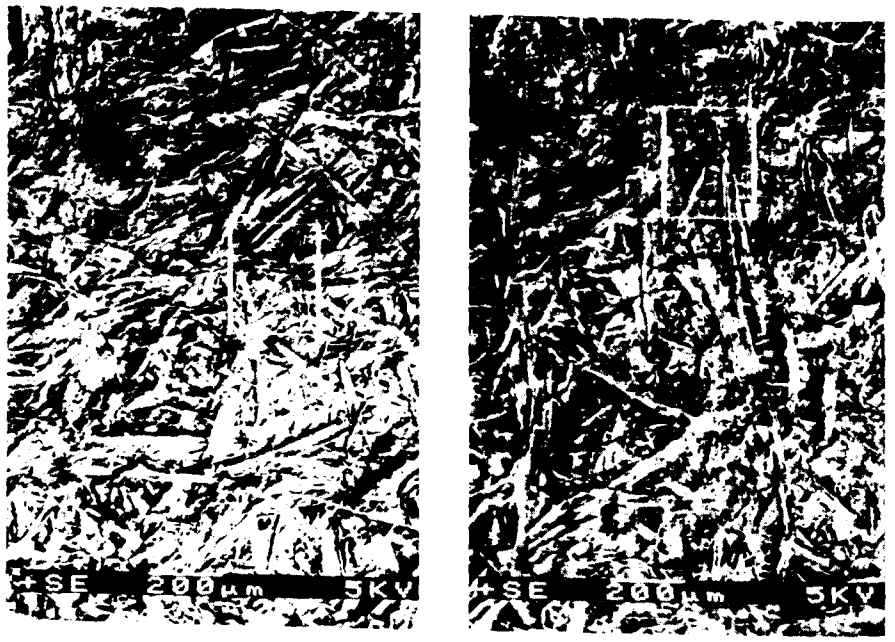

Fig. 2 b: The surface of paper 7 after 185 days exposure to UV-reduced daylight. Magnification factor: 100. Left: washed in methanol (M); right: deacidified (MMC).

paper (Table 7). Whatman chromatographic paper No. 1, comprised only of pure cellulose, and lignin-free high quality writing paper showed no reaction to the deacidification agent. The alkaline reserve $MgCO_3$ produced by deacidification ranged from 3.8% to 9.8% of the paper weight and did not correspond to the degree of yellowing.

As paper samples were exposed to diffused daylight whose UV component was significantly reduced as it passed through the window glass[12], we concluded that the photooxidation reactions observed during light ageing took place only in the lignin component of wood pulp papers and had no significant impact on their saccharidic component (Tables 2–5). Yellowing of the exposed side of both newspaper controls accelerated until the 50th day, a period with a relatively high intensity of falling daylight (September, October). After this period yellowing was considerably retarded and continued quite slowly in the winter season. In the course of 185 days, the brightness of the untreated control samples (C) decreased in modern wood pulp papers (samples 3–6) by 14.4% to 20.5%. In the historic paper (sample 7) the degree of reduction was only 10.2% (Table 3, col. 6). In the deacidified papers yellowing caused by daylight was the most intense until the 50th day of exposure. The total decrease in brightness, however, was slower than that of the control samples. Decrease in brightness of the modern wood pulp papers

ranged from 9.3% to 13.3%. In sample 7, the old wood pulp paper, it was just 5%. The papers decreased somewhat in brightness as a result of deacidification, but deacidified papers became yellowed remarkably more slowly. The brightness curves (Fig. 1) of the controls C and M and those of the deacidified papers start at some distance, but approach each other with length of exposure to daylight and storage. It was even observed that, after the full period of light exposure and storage, the brightness of the deacidified paper was higher than that of the corresponding C and M samples. This effect is most striking with the Slovenka journal paper (no. 3).

During long-term storage of paper in a dark place under suitable storage conditions, we found that yellowing gradually increased in all the papers that had not been deacidified. Since photooxidation reactions were excluded, we considered this to be the result of a reaction accompanying acid degradation of paper: in the deacidified papers brightness was practically unchanged and corresponded to that of both controls. In some cases deacidified papers were even brighter than the controls (Tables 4 and 5). The small change in brightness in the lignin-free samples (papers no. 1 and 2) during exposure to light confirmed that yellowing during ageing is almost entirely the result of changes taking place in lignin; which, because of its chemical structure, can intensively absorb energy in the visible part of the light spectrum[2].

Comparison of the exposed and reverse sides of the paper indicated that the intensity of photooxidation degradation reactions was a result of exposure to direct light. The reverse sides of the control samples of modern wood pulp papers (papers no. 4, 5, and 6) that were not directly exposed to light yellowed more slowly, ranging from 4.6% to 20.3%, than those of the exposed control samples. Paper no. 3 was an exception (Table 5).

The change in brightness of the reverse side of deacidified papers after 185 days of exposure to daylight followed by 5½ years of storage varied: the change was very small in the chromatographic paper (no. 1) and one of the modern newspapers (no. 6), a decrease of 5–6% in the wood free papers and in two of the modern newspapers (nos. 2,3,4) and an increase in the old (no. 7) and in one of the modern newspapers (no. 5). The Mg linkage with lignin structures seemed to be fairly stable. However, the process of natural ageing in deacidified papers was more complicated and obviously dependent on other factors. Probably some magnesium phenolate linkages can split soon after deacidification, releasing phenolic OH groups of lignin. This results in an increase in paper brightness. Photooxidation reactions on the reverse side occurred only to a limited extent and that is why further yellowing did not always occur. Similarly yellowing did not occur on the exposed side of the paper. We concluded that the irreversible photooxidation changes had already occurred and that yellowing was stopped. An in-

Lignins bewirkt eine Vergilbung. Wenn Tageslicht ohne UV-Anteil auf die Oberfläche des Papiers fällt, läuft die davon bewirkte Oxidation deutlich langsamer ab, wenn das Papier neutralisiert ist, was eine langsamere Vergilbung bedeutet. Nach längerem Altern ist der Vergilbungsgrad von behandeltem und nicht behandeltem Papier gleich. Es ist zu vermuten, daß sich der Weißgrad von neutralisiertem Papier während der nachfolgenden Lagerung nicht wesentlich ändert.

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Aqueous Treatment in Pastel Conservation

by RICHARD MOROZ

Introduction

The majority of conservators are hesitant to use water for the conservation of deteriorated pastel paintings because of the extremely sensitive paint layers created by this art technique. Careless treatment causes water stains and changes the colours and structure of the painting.

But is it really dangerous to use water? The early books concerning pastel conservation recommend a bath in water as a form of conservation treatment. Recent experiments confirm this. It is possible to remove certain types of stains and discoloration from pastels using the water bathing process.

Two pastel portraits from the first half of the 19th century, belonging to the Lippisches Landesmuseum in Detmold (Westphalia), were given to the Conservation Laboratory for Paper and Leather Objects at the Westphalian Department for Museums. They were severely deteriorated upon acquisition, and it seemed necessary to use water in the course of conservation. We therefore did a relevant test: Using a picture of little worth and cutting it into two parts, we put one half onto the surface of hot water. Fig. 1 demonstrates that there was no difference to the untreated other half.

The primary type of deterioration with regard to one of the portraits in question was the significant loss of paint layer. In the other, a great number of water stains and holes in the support were to be found. A third pastel portrait came from a small country museum in Rheda (Westphalia). During cleaning the glass housing was broken by the museum staff thus causing the paper support to tear across the face of the portrait.

A Brief History of Pastel Usage

If the term "pastel" is defined as a crayon consisting of powdered pigments without a liquid binding agent, the first known use of pastels may be attributed to the caves of Altamira and Lascaux. However, some art historians have claimed

Restaurator 18: 39–49 © 1997 Saur, Munich etc.

crease in brightness, observable on the reverse side of some of the papers, did not occur on the exposed side.

To determine the actual extent of oxidation changes taking place in paper during natural ageing, we used the carbonyl groups content assignment that is commonly considered to reflect the degree of oxidative changes in paper[8]. Carbonyl groups content was measured after the exposure of the samples to light and a few years of storage. Testing showed that in samples that had not been deacidified, the intensity of photooxidation and other oxidation reactions was significantly higher in those wood pulp papers with a higher lignin content. The old paper (no. 7) had the highest carbonyl groups content. In the paper samples containing lignin we found 11.6 to 28.6 mmol of carbonyl groups to 100 g of paper and 1.29 to 1.63 mmol/1 g of lignin, with the exception of paper no. 4 which had 0.87 mmol/1 g of lignin. These data demonstrate a direct relationship between lignin content and oxidation as expressed by the carbonyl groups content. This relationship was directly connected with degree of yellowing (Table 2,3).

In the course of ageing the papers deacidified with MMC, we found that the oxidation of cellulose also occurred, but to a very small degree[3 8]. This can be seen in the wood-free papers (nos. 1 and 2). Deacidification of paper with MMC retarded oxidation by 39%–50%. Daniels[3] supposes that magnesium as well as other metals of the second group of the periodic system (calcium, barium) have the capability to link free radicals by forming peroxide complexes that block cellulose oxidation. We found that after deacidification, even of groundwood paper with a high lignin content, the extent of lignin structures oxidation as expressed by carbonyl groups content was lower by 31%–48%. This is the main reason that in deacidified samples photooxidation occurs significantly more slowly. We concluded that the presence or absence of acid in newsprint had no decisive impact on the degree of lignin oxidation and brightness reversion of paper during photooxidation. Retardation of oxidation was probably caused by the presence of magnesium ions in the paper or by the reaction of magnesium methanolates with some groups of lignin[3]. The reaction of lignin itself in newsprint deacidified with MMC and subsequently treated with sulphanilic acid demonstrated that a stable linkage of magnesium with phenolic OH groups is formed that significantly retards the course of the most outstanding variable in the oxidation reaction of lignin, i.e., the production of phenoxy radicals.

CONCLUSION

The exposure of wood pulp newspaper to daylight resulted in increased yellowing of paper, this effect occurring most intensively during the first 50 days and reflecting photochemical oxidation reactions of lignin. The yellowing process progressed more slowly during storage under favourable conditions with no light access. Additional yellowing occurring after deacidification of newspaper with methyl magnesium carbonate was caused by a magnesium reaction or by the linkage of magnesium methanolates with phenolic hydroxy groups of lignin. After deacidification the yellowing of newspaper in light is slower, and gradually the difference in brightness between deacidified and non-treated newspapers disappears. The lignin-free papers did not suffer substantial changes. The presence of magnesium either in linkage with lignin or in the form of magnesium ions significantly retarded degradation caused by oxidation and photooxidation reactions. Natural ageing of newspaper deacidified with methyl magnesium carbonate demonstrated that this deacidification procedure can be used for newspaper preservation.

SUMMARIES

Yellowing of newspaper sheets after deacidification with methyl magnesium carbonate.

Deacidification of newspaper with methyl magnesium carbonate results in decreasing brightness. Yellowing is caused by the linkage of magnesium to phenolic OH groups of lignin. If deacidified paper is exposed to sunlight without the UV component, significantly slower oxidation of lignin occurs, which results in slower yellowing. After long-term ageing the degree of yellowing of deacidified newspaper becomes identical with that of untreated papers. We expect that in the course of long-term storage brightness of deacidified papers will not change substantially.

Jaunissement des feuilles de papier journal après la désacidification au carbonate de magnésium méthylique.

La désacidification du papier journal au moyen du carbonate de magnésium méthylique a pour effet de réduire la blancheur du papier. Le jaunissement est provoqué par la combinaison chimique du magnésium avec les hydroxyles phénoliques de la lignine. Lorsque l'on expose la surface du papier désacidifié à la lumière du jour ne comportant pas d'ultra-violet on assiste à une réduction significative de l'oxydation de la lignine, ce qui entraîne un ralentissement du jaunissement. Après un vieillissement à long terme le degré de jaunissement du papier journal désacidifié devient identique à celui du papier non traité. On suppose que la qualité du blanc des papiers désacidifiés ne se modifiera pas substantiellement pendant le stockage à long terme.

Vergilbung von Zeitungspapier nach der Entsäuerung mit Methylmagnesiumcarbonat.

Die Neutralisierung von Zeitungspapier mit Methylmagnesiumcarbonat führt zu einem Rückgang des Weißgrades. Die Verbindung von Magnesium mit phenolischen Hydroxylgruppen des

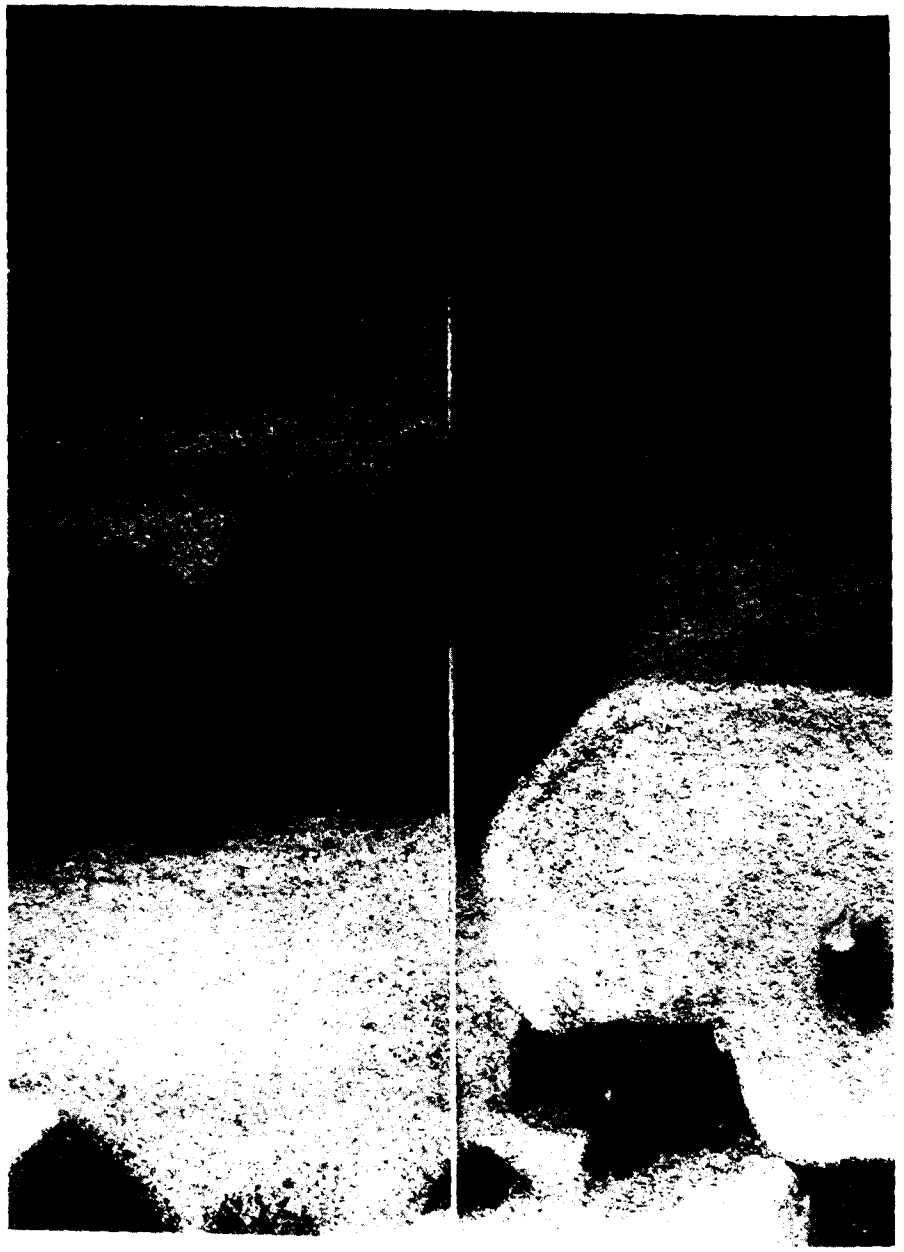

Fig. 1: A pastel divided into two parts, one of them treated in hot water, the other untreated

that the technique of pastel is not based on the use of natural pigments but on those obtained artificially from chalk, gypsum, and a binding agent. Defined as such, pastel use was unknown until the beginning of the 16th century and has been connected to Leonardo da Vinci.

In Rubens' heyday pastel techniques were being used in France, Holland and England, but the filler used in the Continent was different to the chalk filler employed in England. Crayons by today's definition of the term were brought into use almost simultaneously in France (Viven), Poland (Heid 1685), and Germany (Thiel 1697) during the 17th century. While pastels have always been linked to the Rococo period and were estimated quite highly at that time and frequently used, this high reputation decreased, just for portraits, during the first half of the 19th century. The literature of that era, however, is devoted to both Leonardo and Rubens, and the development and conservation of pastel paintings. In the second half of the century, techniques incorporating pastels witnessed a substantial boom in popularity during both the Impressionist (e.g., Degas) and Secession (Jugendstil) movements.

A SHORT OVERVIEW OF THE FEATURES OF PASTEL PAINTING TECHNIQUES

The best results are achieved when pastels are applied to a rough surface. Artists in earlier periods used parchment and paper with varying degrees of roughness to which the pastels adhere easily. During the 18th century the supports of canvas paintings were occasionally covered with an undercoat (e.g., by the Danzig artist Wessel). These supports were then tightened on painting stretchers. Another appropriate support for pastel painting would be paper with cardboard, but this was rarely used. Frequently, the supports of the painting would be roughened with a powder containing quartz (fine sand), marble, pumice and pigments. Pigments otherwise used for tempera paints were used in the production of pastels. Due to their resistance to light, mineral pigments were often preferred.

Traditionally a pastel should contain a small amount of binding agent (e.g., gum solution): sufficient to produce small bars, i.e. crayon. But as this binding agent does not always adhere effectively to a painting's support, some pastels are water-based. Numerous colours are created by mixing a specific quantity of filler such as chalk, zinc oxide, gypsum or white clay with a single pigment. Depending on the proportions involved, varying intensity in colour can be obtained.

Before application of the pastels, the object or subject to be depicted was generally sketched in crayon, black pencil or red chalk. Use of graphite pencils was, however, avoided. The paints were then applied in either a stroke or brush-like manner, by smudging the paint with the finger, or with the use of special tools.

Often in the 18th century, decorative and embroidery details were finished with gouache applied with a brush.

The main weakness of pastels is their susceptibility to abrasion. Testing has been conducted in an attempt to overcome this problem and make them more stable. As of yet, however, no satisfactory results have been obtained

A History of Pastel Conservation

The preservation of pastel paintings has been a matter of concern ever since the birth of the technique. Many experiments concerning the fixatives used for the paint layers have been described. The conservation of pastels was first discussed in the 19th century. Of particular interest are a book by Welsch[1] published in 1834, and a book by Lucanus[2], a chemist from Halberstadt, first published in 1828, and revised by Hans Böhm in 1929. The Kopernikus University of Toruń in Poland has conducted detailed research into the technology and conservation of pastel paintings, including the methods proposed by Welsch[3]

In the conservation of pastels, difficult problematic cases point to fat stain and mould removal, as well as dry cleaning. A rub down in order to eliminate mould stains was recommended. Today, extraction of mould growth is accomplished using suction. Oil and fat stains on the other hand were overcome by scattering chalk powder on the reverse side of the painting and then applying pressure. Extremely resistant fat stains were either scraped off or cut out of the painting and then the painting was repainted.

The fixing of pastel paintings was already being described in articles dating from the 18th century, and modern research and experience have verified these early findings. The first known presentation of difficulties involving the method of fixation was done by de Mayerne. Later, in 1684, de Piles made useful contributions to the subject. In 1753, Antoine Joseph was particularly admired for a new method by the Academy of Art in Paris. He placed the picture vertically over a steaming water-based solution containing fish glue, vinegar and alcohol. One of the pictures treated in this manner is by Rosalba Carriera. This method perhaps gave birth to the idea of a spray fixative, first described about 1750. Glues such as gelatine, casein, resins like mastics, dammar, Venetian turpentine, colophonium, shellac dissolved in alcohol, and, later (19th cent.), zapon lacquer were variously recommended. Arabic gum or fish glue dissolved in water and mixed with egg white was commonly used, although occasionally other concoctions were mixed and tried. Another method of stabilization described in early articles and books was to infuse the reverse side of the painting with a solution of fish glue combined with an acid or alcohol or a mixture of the two.

As a result of changes in refraction caused by a fixing agent, the characteristic features of pastel, i.e., its "velvetness" and its freshness, can be lost. Water-alcohol fixatives based on ammonia casein, borax casein, gelatine and rubber alter pastels to a lesser extent. Fixatives based purely on water affect the appearance of pastel paintings the least, though the painting's support can subsequently become susceptible to warping.

The contemporary method of consolidating pastels while preserving their characteristic features and preventing them from warping is to apply water to the painting while it is being lined onto Japanese paper. Research into earlier techniques and modern experience have now made it possible to remove water stains and the products of paper deterioration which produce yellow staining. In several cases a bleaching agent containing potassium permanganate or a similar substance was tested.

The method that protects pastels most effectively is to place them into a suitable frame and cover it with glass. In this way the painting is protected both from dust, changes in humidity and direct contact with hands. According to recent statistics damage to the paper support is often caused by a lack of framing or by poor framing techniques. These are the main reasons why water stains and dust are found on the surface of pastel pictures. Deterioration of the paint layers, so that only pigment powder remains – observed mostly in heavily painted pictures – has been attributed to humidity fluctuations in the glass housing: As a result of humidity the paint layer attaches to the glass. Inadequate glass housing can also lead to mould growth, sometimes over the entire surface of the painting. This problem is also linked to levels of humidity in the (hermetic) casing.

Pastel Paintings Subjected to Conservation Treatment

The three paintings, two from Detmold and one from Rheda, all painted during the first half of the 19th century, were successfully subjected to conservation. The portraits can be securely dated by the attire of the subjects in the portraits. The young lady (Fig. 2) wears a blue dress with a muslin halter neck. The picture shows a belt positioned high around the lady's midriff and her hair plaited in a braid, characteristic features of early 19th century dress. The mature looking man (Fig. 3) in the second portrait from Detmold is wearing a dark green jacket with a slightly bluish tinge – a colour popular in the Biedermeier era, around 1840. The white cloth tied around his neck is another typical feature of the period. Similarly, the Rheda picture (Fig. 4) portrays a mature man in a light brown jacket. The clothes of the two men are comparable.

THE TECHNOLOGY OF THE PORTRAITS

The portrait of the lady was painted on thin white paper of ribbed structure and glued onto cardboard. Underdrawing below the pastel layer has not been found. The hair is done in brown ochre crayon and the face in a fleshy tone. For the area around the neck the unaltered surface of the paper was used, highlighted with delicate lines in black crayon. Layers of blue paint were used for the dress, and with grey and whitening for the background. The distinguishing feature of the painting is the use of the white paper as a form of highlighter, as in water colour painting. The Detmold man was heavily painted on paper containing blue fibres. Here, the technique used during painting is important as the entire painting and its support have been covered with paint. The paper was subsequently attached to a wooden stretcher using adhesive. The similarity between the Rheda portrait and Detmold portrait of a man is striking. In the case of the Rheda picture, the edges of the painting were glued onto a larger piece of paper. The paint was applied thickly to both. Thereafter, the picture, which consisted of a painted surface sheet and a lining sheet, was attached to wooden painting stretchers. As a result of framing the cardboard separating strips, which maintained a gap between the glass and the painting, became glued to the glass. The back of the picture was protected using a small sheet of cardboard whose edges were glued to the back of the frame.

THE CONDITION OF PRESERVATION

Both paintings from Detmold (Figs. 2 and 3) were delivered to conservators in extremely serious condition, although the type of deterioration was different. In the portrait of the lady only 50% of the paint had survived, the remainder having deteriorated. In many areas lumps of paint were visible. These may have been caused by bacteria. Scattered foxing can be seen over the entire surface of the painting. The painting must have been framed and stored at some point during its life time because sudden cracking of the glass caused minute slits and gouges over the entire surface. Subsequently, the damaged areas were repainted using water colours, which have now interfered with the original, causing peeling: a negative consequence of poor painting during earlier conservation treatment. Following repainting the portrait was glued onto cardboard, which served as a *passe-partout*, and was then mounted into a frame and sealed using glass. As complete air-tight sealing around the painting was not achieved, contamination with dust and other impurities resulted.

In the portrait of the man (Fig. 3), the paint was well preserved but the support of the painting had been cut out of its stretcher, which left traces imprinted on the

Fig. 2: A portrait of a lady from the Landesmuseum in Detmold showing numerous foxings and cuts, before (left) and after treatment (right)

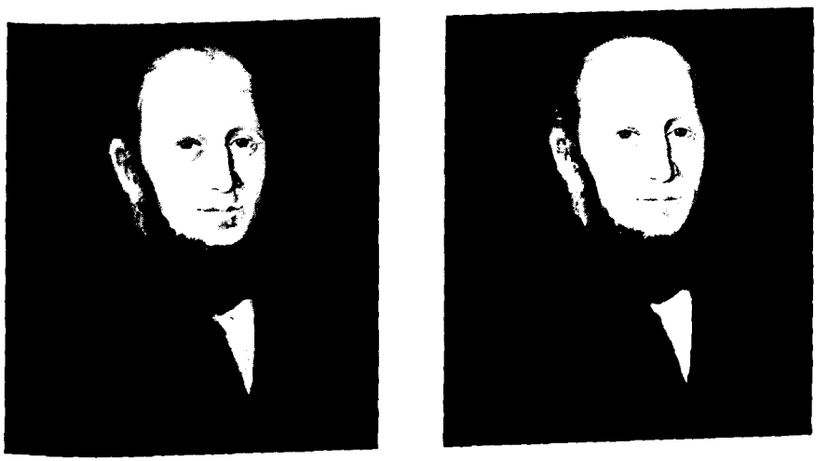

Fig. 3: A portrait of a man from the Landesmuseum in Detmold shows how water stains severely affect the aesthetics of a picture. Before (left) and after treatment (right)

front of the picture. Examination of these traces showed numerous insect holes. During storage the painting must have been placed on its face-up, making it susceptible to water damage which caused substantial staining across the surface. The picture may have been cut away from its stretcher following the water damage and glued onto cardboard at the edges. In the areas of paint loss, the card

Fig. 4: A portrait of a man from the Museum in Rheda before conservation (left side)showing a tear through the face.

board was touched-up with water colours, but as these did not correspond with the original colour of the painting, the un-retouched areas of the picture were painted with a new colour. In this condition the painting was re-mounted on cardboard and stored in a glass housing. In order to maintain a gap between the painting and the glass, strips of cardboard were glued to the edges of the painting using gluten.

The Rheda portrait (Fig. 4) was in excellent condition with the exception of the broken glass casing and the long horizontal tear in both layers of the paper.

Conservation Treatment

Having been removed from their frames, the paintings were cleaned with soft rubber. They were then put face down on a glass panel in order to remove the cardboard backing with a scalpel. After this delicate operation had been carried out, the surface of the paintings were cleaned. Initially, they were sprinkled with powdered rubber of minimum coarseness (0.4 mm), which was then gently blown off. To bleach marks on the portrait of the lady, a 5% hydrogen peroxide solution was applied locally.

During the next phase of conservation work, both of the paintings were subjected to hot water treatment of approximately 70°C, the portrait of the lady being completely submerged and that of the man floated on the surface of the water.

This removed the acidity of the paper along with any stains. Later the reverse side of the paper was sprinkled with mineral water several times, thus giving the paintings a slightly alkaline reserve. Thereafter the painting was smoothed and evened out between sheets of blotting paper and a glass panel. Using a scalpel some of the much larger lumps on the portrait of the lady were removed. Some missing areas and cuts were then repainted with pastel paints dissolved in water.

With regard to the portrait of the man, after the water treatment, small pieces of Japanese paper were glued in the holes of the support using wheat starch. The picture was subsequently placed face down on glass and re-lined on Japanese paper. Its support was moistened with mineral water, and simultaneously wheat starch paste was spread over a larger piece of Japanese paper, which was then placed on the reverse side of the painting and pressed with blotting paper, boards, and stones and left to dry.

The final stage of conservation of this work included primary repainting with water colours, stretching of the painting using stretchers, and a final repainting before mounting into a frame. Placing the painting on new stretchers was necessary. First, the joints in the corners of the stretchers were re-cut so as to enable free movement. Secondly the back side of the stretchers was covered with a polyvinyl acetate water dispersion and allowed to dry. The painting was placed face down on a glass panel and the stretcher was placed on top. The protruding edges of Japanese paper were folded over the back of the stretcher and ironed flat. Instead of wedges that are traditionally used in easel paintings, tightening screws were used. The problems of protecting the painting from dirt and mounting were solved by glueing narrow strips of acid-free cardboard to the edges of a glass panel corresponding to the size of the painting on the stretcher. The glass with the cardboard strips was then mounted into the frame, followed by the picture, which was sealed in with some specially created cardboard. Three pieces of cardboard the outside edges of which were slightly smaller than the external frame size were made. In two of the pieces windows were cut, thus creating two cardboard frames, each equivalent in size to the internal frame. The piece of cardboard placed in between these two had a larger window. The piece cut out was re-inserted between the two smaller pieces, thus creating a sliding door effect. The entire construction was subsequently glued to the back of the frame, enabling access to the stretcher and the tightening screws. This completed the conservation of the portrait.

The picture containing the tear (Fig. 4) required different treatment. As the artist had painted on both the painting and its lining sheet, access to the reverse side of the painting was only possible by ripping away a large area in the lining sheet. The rip line was produced at the point where both sheets met. The piece of lining was subsequently removed. As glue absorbed into the crack would have created a dark line at a later date, minute strips of Japanese paper (ca. 10mm x 3mm) and

wheat starch were used to close the tear. A large piece of paper, sufficient to cover the entire opened area was then glued to the back of the picture using wheat starch. A thin strip of paper placed along the rip line would have wrinkled during drying. The original lining paper was then replaced and the picture framed. The frame serves to conceal the tear from view upon examination of the reverse side of the painting.

SUMMARIES

Aqueous Treatment in Pastel Conservation

Pastels are thought of as water sensitive and therefore as difficult to conserve. The author questions whether they really are. Following a survey of the history of pastel painting – defined as a specific technique – and the history of fixing, which was an important issue from the beginning, the conservation treatment of three typical portraits from the early 19th century is described, all three heavily damaged from earlier restoration and unsuitable storing. Treatment consisted of removing the frames, dry cleaning by sprinkling and blowing off fine powdered rubber, local bleaching, hot water treatment, retouching, deacidification using mineral water, smoothing by pressing under weight, and new framing under glass.

Traitement aqueux lors de la restauration des pastels

Les pastels ont la réputation d'être sensibles à l'eau, ce qui entraîne des problèmes quant à leur conservation. Après un aperçu sur l'histoire de ce genre de peinture - définie comme une technique spécifique - et sur le problème de la fixation des différentes couches de peinture qui s'est posé dès l'origine, on décrit les procédés qui ont été appliqués pour restaurer trois portraits typiques datant du début du 19ème siècle, tous trois gravement endommagés au cours de restaurations antérieures ou en raison de mauvaises conditions d'entreposage. Le traitement appliqué est le suivant: retirer les portraits de leurs cadres; les nettoyer à sec en les saupoudrant de fine poudre de gomme arabique qu'on éliminait ensuite en soufflant dessus; les soumettre localement à un blanchiment, à un bain d'eau chaude, à des retouches; créer une réserve alcaline en les aspergeant d'eau minérale; les lisser en les pressant sous des poids; et enfin les encadrer sous verre.

Naßbehandlung bei der Restaurierung von Pastellen

Pastelle gelten als wasserempfindlich und deshalb als restauratorische Problemfälle. Es wird gefragt, ob sie das wirklich sind. Nach einem Überblick über die Geschichte dieses technisch zu definierenden Bildtypes und des fast von Anfang an auftretenden Problems der Fixierung seiner Farbschichten werden die Maßnahmen beschrieben, denen drei z.T. schwer beschädigte und durch frühere Restaurierungen und falsche Aufbewahrung teilweise entstellte zeittypische Portraits aus dem frühen 19. Jh. unterworfen wurden: Ausrahmen, trockenes Reinigen durch Aufstreuen und Abblasen von feinem Radierpulver, örtliches Bleichen, Heißwasserbad, Retusche, Schaffen einer alkalischen Reserve durch Aufsprühen von Mineralwasser, Glätten durch Beschweren, neue Montage unter Glas.

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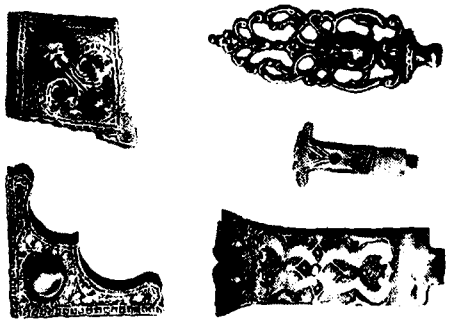

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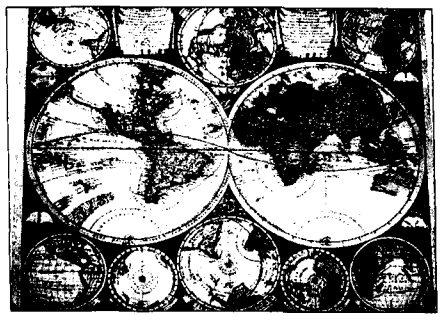

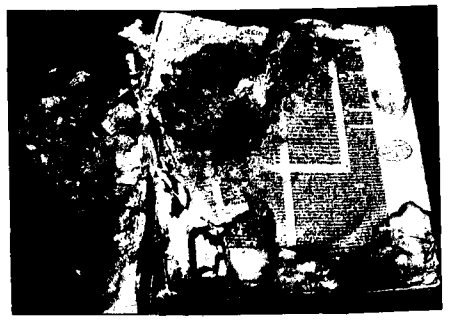

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