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Introduction

by POUL A. CHRISTIANSEN

At the present time there is a widespread interest in the restoration and preventive care of library and archival material, including etchings and drawings. This interest will become increasingly apparent in the years to come.

The growing need for the study of these subjects has led to an urgent demand for publication facilities. As international co-operation is of paramount importance in our time, it seems that this demand may be best met by an independent journal. Many international barriers are being broken down, and more must be broken down, if we are to keep abreast of development, and to maintain high hopes for the future.

This is the background for the publication of RESTAURATOR, the first international periodical covering the fields of restoration and preventive care of library and archival material. It is based on mutual support and co-operation.

Hitherto material dealing with these subjects has been widely scattered in literature, and frequently appeared in journals difficult of access. As this has often proved a stumbling block to scientists, conservators, librarians and archivists in their efforts to keep their knowledge up to date, the end and purpose of RESTAURATOR is to serve as a connecting link, bringing articles based on the research and practical experience of laboratories, as well as of libraries and archives.

RESTAURATOR is open to contributions on all aspects of the subjects in question, provided they are original and well authenticated.

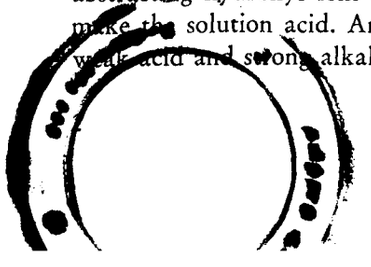
The main part of the journal consists of original papers. In addition, it provides sections for shorter communications, news items, and reviews. Thus, the journal offers an opportunity to everybody interested to follow the progress made in this domain as a whole.

The Non-aqueous Deacidification of Documents

by A. D. BAYNES-COPE

It is well known that cellulose, which forms the fibrous constituent of paper is a polymeric substance and is liable to degradation both by acids and by alkalis. Strong acids cause the links in the polymer chain to break irreversibly and thus eventually reduce the strength of the fibre and of the paper of which it is made. Strong alkalis increase the ease with which cellulose is oxidised with consequent loss of the strength of the fibre. W. J. Barrow[1] has proved conclusively that acid is commonly present in paper, either from alum used in the size, from atmospheric impurities or from ink absorbed and retained by the paper, and that this acidity is one of the major causes, if not the prime cause, of paper degradation. He has been responsible for the pioneer work in developing methods of deacidifying paper. The presence of carbon dioxide in the atmosphere acts as a fairly effective counter to strong alkalis and the problem of excessive alkalinity in paper rarely arises. Barrow suggests that permanent paper should have a pH 6 to pH 8.

It is convenient here to explain what is meant by the terms »strong« and »weak« when these are used in a chemical sense and applied to acids and alkalis. These terms are not to be confused with those describing the order of amount present for which the correct terms are »concentrated« and »dilute«. A »strong« acid or alkali is one which is *completely* ionised in solution to produce respectively hydrogen and hydroxyl ions. A »weak« acid or alkali is one which ionizes in solution to a limited extent and produces a much smaller number of hydrogen or hydroxyl ions in equilibrium with the unionized portion of the acid or base. This theoretical treatment applies to salts too. A water soluble salt, when dissolved in water will ionize completely and if both the acid and alkali moieties are strong, the solution will be neutral as is the case with common salt. If, however, the acid is strong and the alkali is weak, the salt will still ionize completely but the alkali moiety will establish equilibrium with the water present by abstracting hydroxyl ions leaving an overall excess of hydrogen ions to make the solution acid. An analogous reaction occurs with the salt of a weak acid and strong alkali, but in this case the solution will be alkaline.



In chemical notation, for a strong acid and strong alkali:

$$NaCl = Na^+ + Cl^-$$

For a weak alkali:

$$NH_4Cl = NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O = NH_4OH + H^+$$

or:

$$NH_4Cl + H_2O = NH_4OH + H^+ + Cl^-$$

For a weak acid:

$$NaAc = Na^+ + Ac^-$$

where Ac is the acetate radical: CH_3COO^-

$$Ac^- + H_2O = AcH + OH^-$$

or:

$$NaAc + H_2O = Na^+ + OH^- + AcH$$

It should be realized that strength is independent of solubility.

Alum is a mixed salt, usually the double sulphate of potassium and aluminium. Sulphuric acid is a strong acid and potassium a strong base, but aluminium is a very weak base indeed, so that solutions of alum are strongly acid. The principal acid contaminant of air is sulphur dioxide which is fairly readily convertible to sulphuric acid. Thus in deacidification, the problem is to neutralize a strong acid and it can be seen from the above argument that this can be done effectively only by a strong base. It has however also been mentioned that the excess of strong alkali can also be harmful and hence the requirements for an effective deacidifying agent are:

1. It must be a strong base and so form a neutral salt.
2. The unused excess must be readily convertible to a nearly neutral form.

The properties are, fortunately, found in the hydroxides of the alkaline earth metals of which the best known example is calcium hydroxide, for these substances are strong alkalis but are readily convertible by atmospheric carbon dioxide to the white, nearly neutral insoluble carbonates. These carbonates are readily attacked by strong acids. The Barrow method of deacidification is an elegant exploitation of these properties, leading to a controlled method of deacidification.

However, there is one flaw in the excellent Barrow method, for it depends on the use of water and the inks used in manuscripts are often soluble in or readily removed by water. Further, where acid from ink is affecting vellum (which though a protein is destroyed by acid in a manner similar to cellulose hydrolysis) water may not be used because of the softening of the vellum, however permanent the ink may otherwise be.

There is therefore a need for a non-aqueous method of deacidification and there are two choices; a liquid method using an organic solvent or a gaseous method. Experiments both by W. J. Barrow and by the author led to the same conclusion and agreement between both workers, viz that organic bases, the only volatile alkalis, were not strong enough to effect permanent deacidification of paper affected by sulphuric acid. Butylamine, piperidine, and diethylamine were tested by the author and ammonia, *inter alia*, by Barrow, and found to be ineffective in reducing permanently the acidity of paper.

In 1961, the author made experiments with non-aqueous methods of deacidification using bases in organic solvents. Aluminium isopropoxide (as might be expected) was ineffective, for aluminium is a very weak base. In 1961, magnesium methoxide was prepared and shewn unquestionably to be highly effective[2] but the difficulty in preparing and storing this compound, which reacts with water and water vapour very rapidly, led the author to abandon its use in favour of the method described in this communication. The alkali metal hydroxides, though soluble in alcohols, form carbonates which are hygroscopic or efflorescent and are therefore unacceptable, as likely to damage the paper. Calcium hydroxide is insoluble in organic solvents, but barium, a higher member of the alkaline earth series, forms a hydroxide which is more soluble in methanol than in water. Barium hydroxide behaves chemically in a manner very similar to calcium hydroxide in that it is a strong base and forms a nearly neutral carbonate and is, furthermore, readily and cheaply available in a pure form from chemical suppliers.

Accordingly an investigation was begun into the use of methanol solutions of barium hydroxide for deacidifying acid paper. It can readily be understood that the use of this substance as a deacidifying agent is theoretically sound but it was clear that practical tests must be made to establish the truth of this. These tests were directed to the following ends:

1. Did this substance really deacidify acid paper?
2. Did it neutralise acid ink?
3. If an excess was left in paper, was it readily neutralized by atmospheric carbon dioxide?
4. Is paper likely to be harmed by the treatment?

It is not necessary to describe in detail the tests applied, but question 1 was rapidly answered in the affirmative by treatment of acid paper, measuring the pH of the paper before and after treatment.

Typical results, obtained on a 50 year old mechanical wood pulp paper taken from a book, using 1.0% w/v barium hydroxide in methanol are as follows:

	Untreated	*Brushed once**	*Brushed twice*	*Dipped 3. minutes**
Top edge	pH 3.0	5.0	8.4	7.5
Middle	pH 4.1	9.0	9.4	9.8

* pH determined 10 minutes after treatment. i. e. neutralization not complete.

Question 2 was not so easily answered but experiments shewed that the chemical reaction though effective was rather slow compared with the conventional Barrow aqueous method. This is almost certainly due to two facts, that water relaxes cellulose and allows the alkali to interpenetrate the fibres and neutralize the acid there, and that whereas calcium sulphate is more soluble than calcium hydroxide thus being readily removeable from the neutralized area, barium sulphate is very insoluble and would hinder the access of the alkali to the acid area. It was found in practice that neutralization of very acid ink areas on a drawing by Piranesi took about an hour, using 0.2% w/v barium hydroxide in methanol, the change in acidity being from pH 3 to pH 7.

To answer question 3, a strip of thick filter paper was dipped in a solution containing 1% w/v barium hydroxide in methanol and dried quickly. The pH of portions of the paper was measured at hourly intervals and found to fall from pH 10 to pH 8.5 in six hours. If a similar strip was placed in a box with a small lump of solid carbon dioxide (dry ice) the barium hydroxide was neutralized in about half an hour.

For question 4, Whatman No 50 filter paper was used as test paper. (This is an acid washed high strength paper of a texture similar to writing paper). The paper was treated with a 1% w/v solution of barium hydroxide in methanol and with a 1% w/v solution of magnesium bicarbonate in water. The paper was artificially aged by heating at 100° C for 72 hours. The folding endurance of the paper was then determined.

Folding Endurance (No. of folds)

	Control	*Aged*	*Barium Aged*	*Magnesium Aged*
Machine	636	200	502	589
Cross	315	77	171	182

The results shew clearly that barium hydroxide treatment is equivalent to magnesium bicarbonate treatment in its effect on paper. It is not possible to assess the extent to which the loading of the paper, *per se*, has influenced the increase in strength.

The practical techniques of the treatment of acid documents are perfectly straight forward. The solution used in the British Museum Research Laboratory is chosen arbitrarily as containing 1% w/v of barium hydroxide as the free base, made by dissolving 19 g of barium hydroxide octahydrate (the commercially available form) in one litre of reagent grade methanol. It may well be advantageous to use a stronger solution in some cases, where very acid ink has caused gross damage to thick paper or vellum. The solution may be applied by brushing, dipping or spraying and typical examples of these techniques follow.

1. A manuscript music score by Webern on acid paper (pH 4) was deacidified by brushing on the methanolic solution of barium hydroxide. The writing was in good ink and deacidification was directed at reducing the intrinsic acidity of the paper, which was presumably due to acid sizing, without risking any loss of the ink.

2. A large print on thick paper, 60 cm × 45 cm, of little value was mounted on a stretcher. The stretcher was in a frame but the absence of any proper backing left the paper exposed. The turn over was brittle enough to break at a touch and had pH 3.7. It being decided that conventional conservation treatment, (viz, dismounting, washing, bleaching, rewashing, deacidifying, resizing and remounting) was not justified, the print was deacidified by spraying the back of the print with 1% w/v methanolic barium hydroxide. The sum total of sulphuric acid in the paper was such as to make it possible that, were barium hydroxide applied to the front, the barium sulphate would obscure the print and no attempt was made to effect complete deacidification.

3. A paper manuscript, in acid ink, needed both resizing and deacidification. The ink was sufficiently labile to off-set on damp blotting paper and no conventional aqueous method for either process could be employed. The paper was therefore passed through a bath containing 5% w/v of N-methoxymethyl nylon and 1% w/v of barium hydroxide in methanol. Experiments on comparable paper shewed that this would produce a barium carbonate content of about 1.3% w/v in the paper. The paper was dry within about 5 minutes after removal from the bath.

Certain warnings must be given. Methanol is both toxic (T. L. V. 400 ppm) and inflammable (flash point 54° F Abel) and care should be taken when using large volumes and particularly when spraying methanolic solutions. Soluble barium compounds are toxic when ingested and care should be taken to avoid contamination of food stuffs and to wash the hands after using them. Some modern inks and water colour pigments are methanol soluble and care should be exercised when modern documents are deacidified with alcoholic solutions. It is advisable to test the inks with spots of methanol before treatment.

Mr. S. M. Cockerell[3] discovered that an old acid paper deacidified with methanolic barium hydroxide had pH 8 after neutralization of excess alkali by atmospheric carbon dioxide but after about 2 years in a clean atmosphere, the acidity of the paper corresponded to pH 6. The reasons for this would appear to be as follows. Cellulose is oxidised by air, being degraded to, *inter alia*, poly-glucuronic acids. These are soluble in water (forming the »brown ring« of water stains) but insoluble in methanol. In the Barrow process they are washed out of the paper, being more soluble in alkalis than water, but in non-aqueous deacidification they remain in the paper. They would form unstable barium salts which would slowly be converted by carbon dioxide to the free acids and highly insoluble barium carbonate. Such a mixture could have an apparent »acidity« and experiments were made to determine if this could be the case.
10 ml of 0.1 molar solutions of weak acids were shaken with 1 g of A. R. calcium carbonate and the acidity determined.

Acid	*pk*	*pH of 0.1 M*	*pH of 0.1 M + $CaCO_3$*
(Water)			8.4
p-Nitro phenol	7.15	4.4	6.5
o-Chlorophenol	8.85	5.3	7.1
p-Chlorophenol	9.18	6.0	7.6
Phenol	9.89	6.3	7.9
(Alum)		3.3	6.3 (violent effervescence)

Certain other acids were shaken with water and alkaline earth carbonates in sufficient quantity for an undissolved excess of both acid and carbonate to be present. The acidity was determined after standing overnight (3).

Acid	*Water*	*Water* + $BaCO_3$	*Water* + $CaCO_3$	*Water* + *»Magnesium Carbonate«*[1]
CO_2	4.0			7.2
Water		9.1	9.0	10.6
Boric Acid	4.0	6.8	6.9	
Phenol	5.0	7.5	7.5	
Stearic Acid	4.3	6.9	6.8	
Caramel[2] (1 %) ...	6.5	8.4	7.6	9.3

1. »Magnesium Carbonate« (Mag. Carb. Levis B. P.) is a basic carbonate, $3\,MgCO_3\,Mg(OH)_2\,4H_2O$.
2. The sample was 35 years old and chosen as possibly being comparable to poly-glucuronic acids.
3. There appeared to be a consistent error of 0.5 unit in these readings due to a fault in the meter used, and the results are not corrected to allow for this.

Thus it clear that even very weak acids, having a degree of ionisation lower and weaker than carbonic acid can materially affect the apparent alkalinity of suspensions of barium carbonate and calcium carbonate. Sugars form complexes with calcium hydroxide and this may well account for the effect of caramel on the suspensions of the carbonates.

When the major part of the investigations into the use of barium hydroxide in methanol had been completed, the author was advised by Mr. R. Beecher of the Conservation Department of the Victoria and Albert Museum, London, that in 1891, Sir Arthur Church[4] had recommended the use of dilute methanolic solutions of barium hydroxide to deacidify the cloth backing of the Raphael cartoons in that museum, but that was no record of whether or not this had been done. Thus, though the idea was in existence in 1891, this paper is the first account of investigations and practical techniques of using this substance for deacidifying paper and vellum.

Abstracts

The communication describes the use of 1 % w/v solutions of barium hydroxide in methanol for the deacidification of documents in cases where aqueous solutions cannot be used, e. g., for water-labile inks and vellum. Determinations of acidity before and after treatment shew that the method is effective. Folding endurance tests indicate that the method is safe. Experimental evidence is used to explain apparent anomalies in results.

В сообщении описывается применение 1%-ных (по объему) растворов гидроокиси бария в метаноле для раскисления документов в тех случаях, когда не могут быть использованы водные растворы, например, для водорастворимых чернил и пергамента. Эффективность метода была доказана определением кислотности до обработки и после нее. Испытания на сопротивление излому показали, что этот метод безопасный.

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Das Ablösen von Handschriften

von HANS O. SCHÖMANN

Auf zahlreichen Büchern der vergangenen Jahrhunderte findet man Handschriften, Urkunden, Antiphonarblätter und Druckschriften aus Pergament, die als Einbandmaterial verwendet wurden. Besonders nach dem 30-jährigen Krieg war es Brauch infolge von Materialmangel (Schafe, Ziegen, Kälber) altes Schriftgut, das man nicht für bedeutend hielt, zu zerschneiden. Dieses wurde dann oben angeführten Zwecken zugeführt. Für den Bücherrestaurator ist es eine schöne Aufgabe, diese Stücke sorgfältig abzulösen, damit sie für wissenschaftliche Zwecke benützbar sind.

Das Ablösen der äusseren auf dem Einband befindlichen Pergamenthandschriften oder Antiphonarblätter usw. ist verhältnismässig leicht. Eine genauere Untersuchung wird ergeben, dass man die Einschläge des Pergaments (Handschrift) auf der Innenseite des Deckels mit oder ohne Feuchtigkeit ablösen kann. Das so freigelegte Blatt legt man auf eine saubere Unterlage (Löschpapier, Holzpappe oder Glasplatte), auf der aufgeklebten Seite wird sich vielleicht ein festgeklebtes Papier befinden oder Leimreste. Ehe man sie entfernt, hält man das Pergament gegen das Licht und stellt so fest, ob ein Text oder Initialen sich unter dem Papier befinden. Ist dies der Fall, so wird das aufgeklebte Papier mit Weizenstärke (Kleister) angeschmiert. Die Feuchtigkeit des Kleisters wird das Papier durchdringen und den darunterliegenden Leim aufweichen. (Der Kleister sollte dünnflüssig sein). Der Aufweichungsprozess wird je nach Stärke des Papiers und des Leims verschieden sein. Nach einiger Zeit kann man mittels eines Messers das so aufgeweichte Papier abziehen. Nun wird man feststellen, dass auch der Leim aufgeweicht ist, wenn nicht, so muss man mit einem dickeren Kleister kleinere Stellen nachbehandeln. Das Ablösen der Leimschicht erfolgt durch ein Messer. Dies muss sehr vorsichtig geschehen, denn sonst löst man die Farbschicht der Schrift oder Initialen ab. Nun wird jede Stelle ebenso behandelt. Eine restlose Entfernung des Leims wird nicht möglich sein, da dies auf Kosten der Schrift geschehen würde.

Ist die Rückseite behandelt, so dreht man das Pergament um und legt es auf ein Wachs- oder Siliconpapier, damit die Leimreste nicht an der Pappe oder dem Papier festkleben.

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Auf der Vorderseite des Pergaments wird eine Textur sein, die ebenfalls mit Kleister abgelöst wird. Auf dem Pergament wird durch den vielen Gebrauch in den Jahrhunderten das Schriftbild abgegriffen oder stellenweise ganz verschwunden sein. Wie weit hier eine Reinigung geschehen kann, hängt ganz von dem Zustand des Pergaments und der Schrift ab.

Sind die beiden Seiten so behandelt, wird das Pergament zwischen zwei Wachspapiere gelegt und zwischen Holzpappen unter leichtem Druck beschwert. Die restlose Austrocknung erfolgt am anderen Tag zwischen Löschpapier.

Ein Wort zur Farbbeständigkeit der Schrift: Die Erfahrungen haben gezeigt, dass blaue und rote Farben, die längere Zeit der Feuchtigkeit ausgesetzt waren, auslaufen, schwarze und braune dagegen weniger. Mit einem leicht angefeuchteten Schwamm kann man die Schriftfarben von Staub oder Schmutz reinigen. – Auch hier ist Vorsicht geboten! –

Ein besonderes Problem ist das Ablösen von Papierschriftstücken oder -druckerzeugnissen, die als Pappdeckel (Klebepappe) verwendet wurden. Wie bekannt, lösten diese Klebepappen den Holzdeckel als Buchschutz ab. Diese Schrift- oder Druckstücke wurden zusammengeschnitten, aufeinandergeklebt und dienten so als Pappe für den Einband. Sie sind eine Fundquelle für die Makulaturforschung. Wertvolle Urkunden, Handschriften oder frühe Drucke (des 15. und 16. Jhrdt.) wurden auf diese Weise entdeckt.

In den wenigsten Fällen lassen sich die zusammengeklebten Blätter im Trockenverfahren ablösen, das bedeutet dann, dass eine Nassbehandlung durchgeführt werden muss.

Man legt den zusammengeklebten Papierblock in ein Wasserbecken und lässt soviel Wasser hineinlaufen, dass das Papier gut umspült ist. Nach einer gewissen Zeit kann man feststellen, dass das Wasser eine braune Färbung annimt, die Ursache ist der Leim, mit dem die Blätter aufgeklebt sind. Ein Auslaufen der Tinte ist nicht zu befürchten, da die Schrift mit Leim überzogen ist. Ist das Papier gut durchweicht, so legt man den Papierblock auf eine Glasplatte und drückt mittels einer Gummiwalze das überschüssige Wasser aus. Dann erfolgt das Ablösen der einzelnen Blätter.

Man schneidet sich aus einem saugfähigen Papier mehrere Blätter, die die Grösse der abzuhebenden Blätter haben. Eines dieser saugfähigen Blätter legt man auf das erste abzuhebende Blatt, streicht es mit der Hand fest an und hebt mit der Spitze eines Messers eine Ecke bzw. den unteren Rand des Blattes hoch. Nun ruht das erste Blatt mit dem Saugpapier auf der Messerspitze, mit Hilfe des Saugpapiers hebt man es hoch und ab, dann legt

man es auf eine zweite saubere Glasplatte. Mit einem Messer entfernt man auf beiden Seiten die Leimreste, aber nur so weit, dass die Schrift nicht leidet. Die Erfahrung hat gezeigt, dass eine restlose Entfernung des Leimes nicht möglich ist. Die Austrocknung der abgelösten Blätter erfolgt wie beim Pergament. Nach diesem Verfahren hebt man Blatt um Blatt ab. Dass für diese Arbeit ein gutes Einfühlungsvermögen von seiten des Restaurators vorhanden sein muss, ist selbstverständlich.

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The Copper Scroll from Qumran

by JOHN M. ALLEGRO

Towards the end of a ten-week search of the cliffs behind the Essene monastery of Qumran, a party of archaeologists in March, 1952, came upon a cave which had partly collapsed in antiquity. A few potsherds at the entrance first drew their attention to the tumbled rocks that covered the cave. Further investigation produced a lot more pottery of a characteristically Essene style, the fragmentary remains of a score or so of manuscripts, and, in a niche, hard up against an inner wall, two rolls of copper. One was lying on top of the other and had suffered some fracturing of the upper surface, a few small pieces having become detached. These were carefully collected and the surface of the roll treated with a celluloid solution to prevent further disintegration, and the two rolls then separately cleared from the bed of dust and rubble and lifted to safety.

In the Palestine Museum in Jerusalem the rolls were further cleaned and examined. Excitement mounted when indentations visible on the outside showed that the rolls had been engraved with a Hebrew text in letters similar to the palaeography of the already famous and controversial Dead Sea Scrolls. But it was also clear that the opening of the rolls would be extremely difficult. The copper of which they were made had completely oxidized, leaving only a brittle substance that threatened to crumble away at any attempt at manipulation. The sense of frustration among scholars eager for more information about the Essenes and their literature, and among the visitors to the Museum gazing at the rolls in their showcase, was only aggravated by the conclusions of one visiting scholar who decided, from the traces of letters he could read mirror-fashion on the upper surface of the rolls, that they contained a list of buried treasure.[1] He concluded that they might list the communal wealth of the Essene community which, as we know from other documents, pooled all their worldly possessions into a common fund.[2]

With what seems to have been a singular lack of initiative on the part of the Museum authorities, the rolls lay in that tantalising condition for three years. It was clear from the beginning that the only really feasible way of penetrating the document's secrets was by cutting the rolls open. To avoid this somewhat drastic operation, experiments were made in Johns

Hopkins University, Baltimore, by Professor A. H. Corwin, to determine if a replica, reduced to the same state of oxidization, could possibly be reconstituted to its original state of malleability and thus unrolled. The results were, however, not promising, and eventually it was decided to look elsewhere for a solution.

Through the good offices of the Principal, Dr. B. V. (now Lord) Bowden, the resources of the Manchester College of Science and Technology, as it was then called, were offered to the Museum authorities and in 1955 the smaller of the rolls was brought to England and examined in the College's laboratories.

Chemical analysis has already shown that the material had been an almost pure copper, and was now reduced to cuprous oxide and copper oxychloride, with none of the original metal remaining. A line of rivets along the leading edge of one of the rolls corresponded with a matching set of torn holes on the other, indicating that they had once formed a long plaque, some eight feet long and eleven inches wide. Inside the larger of the rolls could be seen a second line of rivets, so that the whole plaque had been made up of three sheets of copper.

It was decided to cut the roll into strips, so planning the cuts that they interferred as little as possible with the writing as far as we could determine the shape and course of the letters from the heavier identations. The operation was put into the hands of the then Professor of Mechanical Engineering, Dr. H. Wright Baker, who set about designing a machine to hold the roll gently but firmly whilst the saw cut through the brittle skin. A steel rod was run through the centre of the roll and then lowered into a cradle running on rails directly beneath a small (1¾") circular saw. Thus the scroll itself moved under the control of the operator, whilst the saw could be lowered gently onto the surface as it passed beneath.

Prior to the cutting, the outside of the roll was cleaned of the archaeologists' coat of cellulose varnish with acetone and then stiffened and bonded with a thin coating of an aircraft adhesive, »Araldite 102«, with a 7% hardener (»Araldite 951«) and a small quantity of toluene to assist penetration. It was then warmed for about three hours in an electric oven to 40–50° C. so that when the saw bit into the surface of our precious scroll it should at least have some protection from total disintegration in its plastic skin.[3]

Nevertheless it was with some apprehension that this completely unique document was laid upon its operating table. We had no means of knowing how the oxide would stand up to the saw, nor, having penetrated the outer

layers of the roll, how far the inner leaves might have bonded themselves together into one solid mass, as had happened with one or two of our parchment scrolls from the Qumran caves.

In fact, the much-feared inner adhesions turned out to be mercifully few, and only in one case had a segment to be removed from its lower neighbour in small pieces and later rejoined. Even then the Araldite backing proved its worth in keeping the pieces as large as possible for the subsequent 'jigsaw-puzzling'.

As far as possible, the cuts were made diametrically opposite one another, but as the inner convolutions were reached, it became necessary to make the cuts to conform with the irregular surface of the material. The rolling of the document had apparently been done in a hurry. This was shown not only by the broken line of rivets that had split the document into two parts, but by the way the end of the scroll had been forcibly bent round to make the first turn, the indentations of the person's thumbs being clearly visible where he had creased the soft metal. Clearly the document had been made to imitate a normal parchment scroll, riveting taking the place of the sewing of the skins, and had been rolled from each end towards the centre in the usual fashion.

The successful cutting of the smaller of the rolls persuaded the Jordanian Government of the effectiveness of the scroll-cutting instrument and its manipulators, and the second, larger roll, arrived in England in the winter of 1955–56. Very soon the whole document lay open, twenty three segments, their message facing the light of day for the first time in two thousand years.

The text had been written in twelve columns, the letters being punched into the soft metal with a small stylus, perhaps ⅛" broad. The scribe had begun each column with fairly well proportioned and spaced letters, but as he reached the bottom of the columns had become tired or cramped and his engraving suffered in consequence. Towards the end of the document his efforts became more and more laboured, and he seems to have undergone a mild panic at the thought that he would not find room on the sheet for the last few items. His letters became badly formed, too lightly indented, and with insufficient space between the lines. In fact, he ended up with a third of a column to spare.

The cleaning of the inner face of the scroll was done first with a small brush, and this removed most of the fine cave dust still clinging to the surface. In the smaller crevices or cracks in the metal and in the indented letters themselves, we found a dental nylon brush invaluable, and where in-

crustation resisted the brush, a small dental burr could be substituted and proved effective. Finally the inner surface of the scroll was washed over with a Perspec solution in chloroform to seal it and prevent further corrosion.

Photographing the concave surface of the segments has presented problems as yet unsolved. It has proved impossible to produce a set of pictures which can be laid side by side to give at one glance an accurate impression of the whole text. To see some of the more lightly engraved or badly preserved characters it is necessary to turn the segment this way and that to the light, and such marks are extremely difficult to reproduce in photographs. The best that can be done to aid the scholar who has not access to the original, is to present him with a portfolio of scores of separate pictures, with sometimes half-a-dozen differently angled shots of each segment. Even then, any reading based on photographs alone is bound to be only tentative.

Dr. Kuhn's suggestion about the nature of the scroll's contents found few supporters. Lists of treasure trove among the serious religious works from Qumran seemed, to say the least, unlikely. Nevertheless, Kuhn was right. As the segments came from the machine and were laid side by side on the laboratory bench, the message became clear.[4] In all, some sixty items of treasure, buried in various places in Palestine, were listed. As well as bars of gold and silver, there were hundreds of sacred vessels named, showing clearly that the hoard came from some religious treasuries, presumably those of the Jewish Temple in Jerusalem. There was also a scroll or two referred to, and jars of essences or tithes, the nature of which it is still impossible to determine.

The question still remains open: is the list a genuine treasury inventory, or make-believe? One of the difficulties scholars find in accepting its authenticity is the vast amounts involved, perhaps as much as four-and-a-half thousand talents in weight, apart from the precious metals contained in the sacrificial vessels. As I pointed out in the *editio princeps*,[5] however, we cannot be sure about the precise significance of the *kikkar*, »talent«, of the scroll, and not all of the items are of such large amounts.

Again, whilst it is true that the fanciful disposal of the treasures of the Solomonic Temple forms a favourite theme of Jewish traditions,[6] nothing among such literature matches the matter-of-fact inventory of our scroll. Take, for instance, Item 25: –

»In the tomb which is in the Wady *Kippa*, on the way from Jericho to Secacah, buried at seven cubits: 32 talents.«

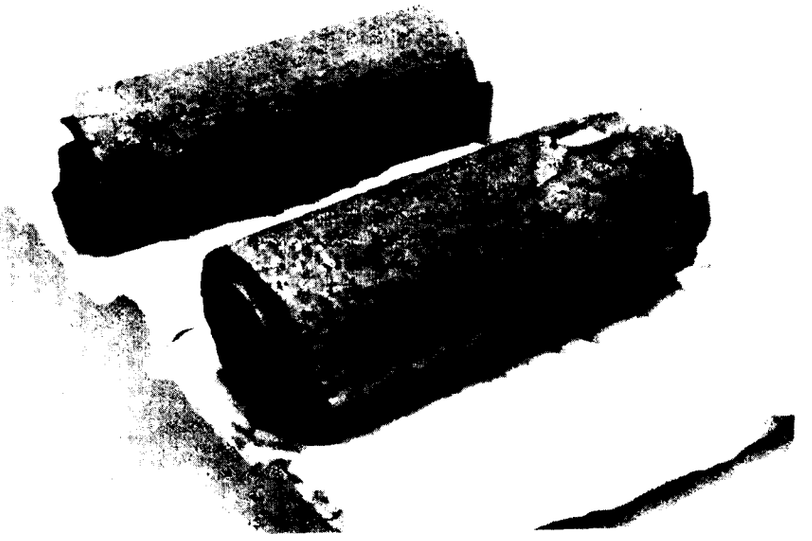

Plate 1. The copper scroll before opening

Plate 2. Dr. H. W. Wright Baker cutting the copper scroll

Plate 3. Open segment of the scroll

Beginning of the scroll *Line transcription*

Secacah is only mentioned once in the Bible, among the so-called 'Cities of the Wilderness' (Joshua xv, 61), but appears a number of times in the copper scroll. Incidentally, there seems good reason for equating it with Qumran itself, where, indeed, a small treasure hoard was discovered by the archaeologists.

If the inventory is entirely fictitious, one must ask why anyone should have taken such trouble to compose it in such realistic terms, and why engrave it laboriously, if not very expertly, on sheets of pure copper. Some think it may have had a cultic use,[7] which is certainly possible, although in that case one might reasonably have expected some more artistic presentation than the rather crude and hurried effort of our scroll.

Again, the kind of treasures that feature in most of the traditional accounts, do not appear in our scroll. For instance, there is no mention of the seven-branched candlestick, a favourite symbol of the Temple cultus. This is not surprising if the inventory refers to the treasures of the Second Temple of King Herod, for those articles which remained in use in the sanctuary up to the time of the pillaging by the Romans in August, A.D.70, are featured among the loot portrayed on Hadrian's Arch in Rome.

In short, it is possible to work out a feasible connection between the treasures of the copper scroll and the dramatic events of the 66–70 Jewish revolt, and one scholar indeed uses the scroll to support his belief that the people of Qumran were not Essenes but Zealots, backbone of the anti-Roman movement.[8]

I myself find it difficult to disassociate the scroll from this cave at Qumran with the sectarian literature found nearby in the same cache and in other caves in the vicinity. Certainly the archaeological evidence is inconclusive. At the same time, we have yet much to learn about the Essenes and Zealots, and there seems good reason to think that we have hitherto been altogether too naive in our reading of the Dead Sea Scrolls, as indeed, of the New Testament. We have failed to appreciate the secret nature of the movement, and too ready to take the writtings at their face value. The final answer on the copper scroll must await a much fuller understanding of these associated mystery cults.

Summaries

In 1952 archaeologists working in the vicinity of the Essene establishment at Qumran, by the shores of the Dead Sea, came upon a partly collapsed

cave. Inside were discovered parchment scroll fragments, of the kind already found in caves in the vicinity, and with them two rolled-up strips of copper, long ago completely oxidized and extremely brittle. Cleaning revealed traces of a Hebrew script engraved on the inner surface, but insufficiently clear to ascertain the nature of the strange and unique document. After some three years of deliberation, it was decided to cut the strips into segments and this was done in the laboratories of the Manchester College of Science and Technology, England.

The twenty-three segments that were successfully separated revealed the whole text of the document, but even now there is no real consensus of opinion on its true significance. It clearly purports to be a list of buried treasure, the sacred wealth of the Jerusalem Temple, but some scholars have doubted its validity, placing it in the genre of folk-tales which abound in Jewish traditions concerning the disposal of the Temple treasures. Others find it far too realistic to fall into this category, despite what appears to be the vast amounts of precious metals involved. Probably the final answer must await further elucidation of the nature of the Essene community of the Dead Sea Scrolls and its relationship to other similar mystery cults of the period.

В 1952 г. археологи, работая около хозяйства общины ессеев в Кумране на берегу Мертвого моря, случайно нашли частично разрушенную пещеру. Внутри были обнаружены фрагменты пергаментых свитков, подобных тем, которые уже не раз находили в пещерах поблизости. Вместе с этими свитками были найдены две свернутые полосы из меди, которые давно полностью окислились и стали чрезвычайно хрупкими. Очистка обнаружила следы гравированного текста на древнееврейском языке на внутренней стороне свитка, недостаточно отчетливые, чтобы установить характер необыкновенного документа. После примерно трех лет обдумывания было решено разрезать полосы на сегменты. Это было сделано в лабораториях Манчестерского технологического колледжа, в Англии.

Двадцать три сегмента раскрыли полный текст документа, но и теперь нет единого мнения об его истинном смысле. Повидимому, это перечень сокровищ клада из сакральных ценностей Иерусалимского храма. Некоторые ученые сомневаются в его подлинности и связывают документ с обычными в иудейской традиции народными легендами о храмовых кладах. Другие авторы находят, что документ слишком реалистичен для такого объяснения, несмотря на то, что в нем фигурирует огромное

количество драгоценностей. Вероятно, окончательный ответ последует за дальнейшим изучением общины ессеев, которая создала свитки Мертвого моря, и ее связей с другими тайными культами этого периода.

NOTES

1. K. G. Kuhn: *Les rouleaux de cuivre de Qumran.* Revue Biblique 61 (1954): 193–205.
2. Cf. 'Manual of Discipline' vi 19–20 in *The Dead Sea Scrolls of St. Mark's Monastery,* vol. 2 fasc. 2. New Haven 1951.
3. For Dr. Wright Baker's own account of the work of cutting the scroll, see *Notes on the Opening of the »Bronze« Scrolls from Qumran,* in Bulletin of the John Rylands Library 39 (1956–57): 45–56, ill.; and his contribution to *Discoveries in the Judaean Desert of Jordan,* vol. 3: Les »Petites Grottes« de Qumran. Oxford: Clarendon Press 1962. Pp. 203–10.
4. For an account of the initial decipherment of the text, see John Allegro: *Treasure of the Copper Scroll.* New York: Doubleday & London: Kegan Paul 1960 & 1961. Revd. ed. New York: Anchor Books 1964. Chapter 2.
5. *Op. cit.* pp 58 ff.
6. For examples, se *op. cit.* chapter 3, and J. T. Milik in *Discoveries in the Judaean Desert of Jordan,* vol. 3: Les »Petites Grottes« de Qumran. Oxford: Clarendon Press 1962. Pp. 275 ff.
7. E. g., see H. E. Del Medico: *The Riddle of the Scrolls.* London: Burke 1958. Pp. 187 ff. (Eng. vers. of *L'Enigme des Manuscrits de la Mer Morte,* 1957, transl. by H. Garner).
8. G. R. Driver: *The Judaean Scrolls.* Oxford: Blackwell 1965. Pp. 30 ff.

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Softening and Restoration of Parchment in Manuscripts and Bookbindings

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When leather is stored for a long time it undergoes physical and chemico-physical changes which gradually destroy it.

These changes take place with time, and first and foremost depend on the tanning and processing to which the leather has been subjected, and the storage conditions, etc. Thus, old russet-tanned leather is apt to be oxidized in contact with air (oxidation of tannides) and to absorb sulphurous gas (SO_2) from the air. Therefore such leather will become brittle and fragile, and be easily pulverized.

The aging of parchment takes place differently, as the molecular peptide chains in the collagen of parchment are not bound by the molecules of the tanning agent, and the structural elements are not protected by tanning agents. Parchment is less resistant to all kinds of changes in temperature and in the moisture content of the air. The grain side of the parchment is more resistant to oxidation by the air, and because of its specific treatment, it is not destroyed by the sulphurous gas of the air.

On the grain side, the aging of all sorts of leather becomes apparent when fragility, brittleness, buckling and deformation sets in.

Such changes also take place in parchment in the course of time. The processes of buckling and deformation are especially apparent.

Evidently the deformation of parchment is dependent on the fact that during long-term storage, parchment, like any other leather, loses its moisture, as its capacity for absorbing the moisture from the air is reduced, i.e., its hygroscopic properties are reduced. This process of dehydration in leather is constant.[6] Therefore, the distances between the polypeptide chains in an albumin molecule are reduced, and the interaction between these chains is intensified.

An intense interaction takes place between the links of a polypeptide chain. This interaction is brought about by numerous hydrogen couplings of nonpolar couplings, and of salt couplings. The hydrogen couplings are of fundamental importance.

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When dry, the sidechains of an albumin molecule are in a deformed and somewhat stressed state. As the collagen is moistened the tension is gradually reduced and due to this the chains are straightened.

The highest degree af orientation of the sidechains is reached when the mutual influence of the chains is completely weakened by the water separated from a molecule and adsorbed by the collagen.[1,2] The deformation and buckling of parchment is also dependent on the fact that the collagen fibres and the substance between the fibres, which give the material its original, characteristic appearance and are the basis of its strength, react in different ways to the changes in the moisture and temperature of the surrounding air. [8,16]

A series of ensuing changes in the humidity and in the temperature of the air, varying from increased values to low values, determine the deformation of parchment leaves.

Restoration of the original properties of parchment is a very difficult task.

The difficulty is due to the fact that when softening and restoring the parchment, the text and the figures on the parchment are liable to damage, and these embellishments are generally unique and extremely valuable. Some parchment manuscripts may have existed for more than a thousand years.

Already before our era parchment was used as writing material.

According to Pliny in the second century before our era, the Egyptian rulers prohibited the export of papyrus, as they wished to maintain the riches of the library at Alexandria. In Pergamum (Asia Minor) attention was drawn to leather called »Difteri« used for writing in Persia and Greece. »Difteri« was improved and thus was obtained a more suitable writing material called parchment. For a long time the new material competed with papyrus, though it was more expensive than the latter.

In the Roman Empire parchment was preferred to papyrus for various state documents. In the monasteries papyrus was used for religious books and holy writings.

Parchment was far stronger than papyrus. Both sides of it could be used for writing, and it was possible to correct the written text.

Gradually papyrus was superseded by parchment practically everywhere. It was produced in France and in Greece from sheepskin, goatskin and calfskin. The best parchment for writing, vellum, was obtained from the skin of very young calves (in French: »Velia«, from which is derived the name of this type of parchment).

Parchment was produced in white and violet colours; Indian ink, gold and silver were used for writing on it.

At the present time parchment is produced in small quantities in France, Czechoslovakia, Germany and Great Britain, where it is used for state documents, for musical instruments (drums, etc.), and for bookbindings.

There are three sorts of parchment: one used for writing, i.e. vellum, and the other two for musical instruments and bookbindings.

Parchment for bindings and instruments is made from the skins of rams, goats, calves, asses and pigs.

The skins of calves and lambs not more than 6 months old are used for the production of parchment for writing. In Russia parchment was made from animal skin in the 15th century, when it was used for state documents and for holy books.

In 1850 parchment was produced by Mikheev in St. Petersburg. At the same time, the famous parchment craftsman Revin was working in Moscow.[8] Parchment production was a handicraft akin to art, and the tradition was passed on from generation to generation.

After removal of the upper layer the hide was washed and stretched while still wet on wooden frames, where it was fixed with pins or nails and smoothed in order to remove any creases or wrinkles. When the shreds had been removed from the hide, chalk was applied to it on both sides, and the surfaces were lightly rubbed with pumice in order to press the chalk into the skin and moisten it.

The quality of the pumice and the rubbing of the skin with pumice are of great importance. The parchments produced in Strasbourg were considered to be the best. They were used for water colours and oil-paintings (Van Dyck and others). The excellent quality of the Strasbourg parchments was ascribed to the polishing with pumice and the quality of the pumice used. The careful way in which all operations were carried out, and the properties of the hide were also important factors. Parchment does not require a thick layer of chalk. The white skin should be used for the front of the parchment, and only the very finest layer of chalk should cover the pores and the fibres of the skin, so that the skin is used for writing and not the chalky layer.[8]

From a chemical point of view parchment, like any other leather, is a complex material created on the basis of the derma of animal hide. The derma consists of albumins, the basic albumin being the animal albumin collagen. Besides albumins, parchment contains a considerable quantity of substances that maintain its elasticity (water and oils). Unlike the russet-

tanned leather of the bindings of old books, parchment is an untanned, depilated skin, a naked skin consisting of the fibrous tissue of natural albumin of collagen, and a gelatinous, gluing substance found between the fibres, which consists of a long series of simple and complex albumins (mucins and mucoids). The substance found between the fibres is also called the cementing agent. When it dries out, the interfibrous substance becomes a hard, transparent, gelatinous mass which forms an obstacle to the free movement of fibres and fibrils in relation to one another. The cementing agent has a gluing effect only in dry skins and here it gives the raw material a parchment-like appearance, and lends strength and stiffness to leather. Partial or complete removal of the cementing agent and the penetration of tanning substances into the fibres and even into the fibrils protect them from sticking together when tanned leather is dried. The fibres are able to move freely in relation to one another and the leather becomes supple. For untanned, naked skin, as for instance parchment, the conditions are different. In parchment, the fibres of the collagen are glued, they are cemented by the interfibrous substance, and therefore parchment is hard and inelastic. It is well-known that naked skins are more liable to damage and decay than tanned-leather, i.e. parchment is more swiftly destroyed than paper by humidity. This is explained by the fact that parchment fibres undergo no processing, and are not chemically bound by tanning substances. The fundamental task in the restoration of parchment is the softening and the straightening of the dried-out, cemented and sometimes horny leaves. In practical restoration work several methods may be used for softening the parchment. These methods are far from perfect and quite complicated, and an evaluation of the effect of the substances used on parchment is founded exclusively on organoleptics. Thus Professor N. I. Pikhonov has recommended the processing of parchments with a mixture of glycerine, water and alcohol in the relation: 1:1:1.[14]

For the softening of parchment, P. Ya. Mizin[10] recommends an 0.12% spermaceti emulsion of the following composition:

1. 96% alcohol: 95 ml
2. Glycerine: 2 ml
3. 4% spermaceti in benzene: 3 ml

The Leningrad Laboratory for the Restoration and Conservation of Documents at the Academy of Sciences of the U.S.S.R. has used two methods for the softening and restoration of parchments.

According to the first method the parchment is moistened in a chamber for 6–24 hours, and then the moist parchment is stretched on a panel or on a frame and fixed with nails for 24 hours. Whereafter the parchment is pressed between sheets of filter-paper and cloth.

In the second method the parchment is first moistened in a chamber, and then processed by means of an egg softener or a lanolin emulsion and is straightened out on glass. After partial drying on glass, the parchment is pressed between sheets of filter-paper and cloth.

The composition of the egg softener is:

1. Yolk of egg	30–40 g
2. Glycerine	20–30 ml
3. Distilled water	20–30 ml
4. Ammonia	3 ml
5. Spirit of soap	10 ml
6. 96 % alcohol	60–70 ml
7. Thymol: 2 % of the whole mixture	

Pharmacologically the lanolin emulsion is:

1. 96 % alcohol	50 g
2. Distilled water	100 g
3. Lanolin	5 g
4. Glycerine	10 g
5. Neutral soap	2 g

The M. E. Saltykov-Shchedrin Library in Leningrad has moistened parchment with distilled water in order to straighten it out. The distilled water was applied by means of filter-paper, whereafter the moistened parchment was pressed.

In other countries no methods of parchment softening are used.

In his book *»On the Preservation of Leather-bindings and Old Manuscripts«*, Dr. Plenderleith, the Director of the Research Laboratory of the British Museum, recommends rubbing parchments with water in order to remove dust and grease, and then drying them swiftly near an open window or in a fume hood.

This is also the opinion of Langwell.

Plenderleith and Langwell[22, 23, 24, 25] are of the opinion that it is of fundamental importance to the preservation of parchments that normal preservation conditions are created. We also feel that normal conditions of preservation (air temperature 16–18° C and relative moisture of the air

50–65 %) are of paramount importance to the preservation of parchment, as well as of all other cultural treasures.

Restoration and softening are prerequisites in the treatment of materials which have been damaged by incorrect preservation, for instance by excessive temperature, by over-illumination of the depository, or by too much or too little air humidity.

By parchment softening is meant the restoration of the original properties of the parchment.

Before we began to elaborate the methods for the softening and restoration of parchment, the existing methods of softening were tested and several essential deficiencies were found. Thus, processing of parchment with glycerine makes it sticky and increases its hygroscopicity by 150–200 %, and the material will easily become mouldy.

Mizin's method of processing parchment with an 0.12 % spermaceti emulsion is correct in principle, but the concentration of spermaceti is so low that practically no softening is obtained.

By using a lanolin emulsion a considerable degree of softening is obtained, however, work with this emulsion involves the risk that the text may be damaged, and the parchment become transparent due to the effect of the lanolin. The same risk is present when processing parchment with egg emulsion, which may damage the text. The latter may also be destroyed by micro-organisms, since an egg emulsion, which is a water-containing emulsion, can be a very suitable medium for the development of mildew and bacteria.

We did not attempt to solve any theoretical problems. – The purpose of our work was to find a method of softening which would remove the deformation of old parchments. We tested a series of substances: glycerine, water, ethyl alcohol, sorbitol, a spermaceti emulsion, an egg emulsion, a lanolin emulsion, sodium acetate, lactic acid, dibutyl phthalate, dioctyl sebacinate, lavender oil, a water solution of urea, and an alcohol solution of urea.

Table 1 gives the physical and mechanical properties of new parchment after processing with the substances mentioned above. The facts indicated show that processing with water does not soften parchment. After processing with water, parchment becomes stronger, but it also becomes harder. The limit of strength of non-processed parchment is 3.02 kg/mm². After processing with water, it is increased to 5.27 kg/mm². The hardness is increased from 1434 kg to 2200 kg. Processing with alcohol only gives an insignificant increase in strength as well as hardness. The limit of strength in-

Table 1

The effect of various substances on parchment (new parchment)

Samples of new parchment processed	Directions	Average thickness in mm	Average breadth in mm	Cross-section in mm^2	Load at a tension of 1 kg/mm^2	Elongation in mm at a tension of 1 kg/mm^2	Load at rupture per 1 kg	Elongation at rupture in mm	Limit of strength in kg/mm^2	Module of elasticity in kg/cm^2	Hardness in kg	Relative elongation in %
Control	Along	0.215	10.90	2.31	2.31	0.67	7.68	5.77	3.29	6 000	1 434	1.76
	Across	0.233	11.20	2.47	2.47	1.10	8.20	6.25	2.75			
	Average	0.229	11.05	2.39	2.39	0.88	7.94	6.01	3.02			
Water	Along	0.199	10.60	2.11	2.11	0.47	10.95	4.55	4.91	10 000	2 200	1.08
	Across	0.251	10.70	2.30	2.30	0.62	12.90	7.56	5.64			
	Average	0.225	10.65	2.20	2.20	0.54	11.92	6.05	5.27			
96 % alcohol	Along	0.201	10.50	2.12	2.12	0.90	5.70	3.48	2.70	7 500	1 590	1.44
	Across	0.206	10.30	2.13	2.13	0.55	8.00	3.70	3.74			
	Average	0.203	10.40	2.12	2.12	0.72	6.85	3.59	3.23			
Glycerine	Along	0.475	9.90	4.70	4.70	16.50	3.45	17.05	0.73	303	164.2	33.00
	Across	0.652	9.40	6.15	6.15	16.50	2.32	11.95	0.57			
	Average	0.563	9.65	5.42	5.42	16.50	2.88	14.50	0.55			
1 % solution of sodium acetate	Along	0.194	10.40	2.00	2.00	0.72	10.30	4.40	4.68	7 500	1 460	1.86
	Across	0.234	10.20	2.49	2.49	0.75	11.20	5.20	4.54			
	Average	0.214	10.30	2.24	2.24	0.73	10.75	4.80	4.61			
20 % water solution of urea	Along	0.223	10.50	2.35	2.35	0.90	9.55	7.85	3.74	5 000	1 205	1.86
	Across	0.223	10.50	2.48	2.48	0.96	9.30	7.45	3.36			
	Average	0.223	10.50	2.41	2.41	0.93	9.42	7.61	3.55			
10 % alcohol solution of urea	Along	0.218	10.20	2.23	2.23	0.92	10.90	4.80	4.87	5 000	1 175	1.84
	Across	0.233	10.70	2.48	2.48	0.93	9.68	4.96	3.87			
	Average	0.225	10.45	2.35	2.35	0.92	10.29	4.88	4.37			
Spermaceti emulsion (according to Mizin)	Along	0.292	10.40	2.42	2.42	1.03	4.40	6.05	2.38	6 000	1 386	1.70
	Across	0.220	10.00	2.20	2.20	0.67	6.30	5.10	2.70			
	Average	0.256	10.20	2.31	2.31	0.85	5.35	5.57	2.54			

creases from 3.02 kg/mm² to 3.23 kg/mm², while the hardness increases from 1434 kg to 1590 kg.

Processing with acetic acid sodium also increases the strength and the hardness.

Dibuthyl phthalate, diotyl, sebacinate and lavender oil make parchment greasy and transparent.

Processing with glycerine greatly softens parchment and makes it elastic, but the strength is reduced hereby. Thus, the hardness is reduced ten times, and the strength is reduced six times in comparison with the control samples.

Samples of new parchment processed with glycerine will in moist air become sticky and viscous, and be transformed into a gelatinous substance. A spermaceti emulsion prepared according to the method of P. Ya. Mizin has a slightly softening effect.

According to our facts, the best results are obtained by processing parchment with a 10% alcohol solution of urea. Processing with the alcohol solution of urea does not destroy the text, nor does it damage the colours of the illustrations and maps. As compared with other substances which we have tested, urea has the advantage of not being hygroscopic, and therefore it will not make the parchment sticky, as in the case of glycerine. Urea may be dissolved in alcohol, which offers the possibility of avoiding a water medium when restoring parchment. This is favourable for the preservation of text and drawings. In addition, it is known from the literature that processing with urea affects the local bonding, and causes no harm.[4]

Urea is a polar substance. It interacts with the polar groups of collagen and weakens the interaction between the polypeptide chains. In this way it helps to unfold the folds in albumin molecules. Urea separates the polypeptide chains, thus increasing the distance between them, whereby hardness is reduced, and deformation is removed.[2]

Old, dried-up deformed parchment which has been processed with a 5–10% solution of urea in 50% alcohol, becomes elastic and loses deformation.

Figs. 1 and 2 show a book made of parchment, Ptolemy's »Geography« published in 1511, before and after processing with a 10% alcohol solution of urea and ensuing greasing with a 2% spermaceti emulsion (an alcohol-benzene emulsion).

The leaves of the book were very badly damaged and part of them were stuck together making the book impossible to use. Five years have passed since the book was restored and it is still in good condition.

For our experimental work we used four types of parchment: new parchment (goatskin) which was produced by the experimental factory of the Central Scientific Institute of the Leather and Footwear Industry; old binding parchment from the 17th century (calfskin); old writing parchment (vellum) from the 17th century and old binding parchment (pigskin) from the 18th century.

In order to control the effect of urea on parchment, careful analyses were carried out of all the above-mentoined parchments. They were processed with a 10% alcohol solution of urea and also with a 10% solution of urea, after which followed greasing with a 2% spermaceti emulsion.

The analysed samples were stored for 18 months after processing. Some of the samples were subjected to artificial aging (10 hours irradiation by a mercury-quartz lamp of the type PRK-2 at a distance of 25 cm).

In order to elucidate the physico-chemical properties of the skin, the following data were obtained by aid of a Shopper dynamometer:

1. The load at rupture
2. The elongation at rupture
3. The relative elongation
4. The limit of strength
5. The elongation at a load of 1 kg/mm^2
6. The hardness and module of elasticity at stretching

All the experiments were carried out on groups of parchment samples, according to the classical method, composed with an asymmetric fringe.[9]

On the basis of the physico-mechanical analysis of old parchment (binding parchment and writing parchment) as well as of new parchment which was stored for 18 months after processing, we found that processing with urea and spermaceti emulsion did not reduce the strength of the parchment at rupture. The elongation was increased after processing, and the hardness usually decreased. The same phenomena were observed after artificial aging.

The strength of new parchment at rupture (see table 2) is not reduced after processing with a 10% alcohol solution of urea. In the control samples the load at rupture was equal to 10 kg. In the samples processed with urea it was equal to 10.06 kg. The limit of strength is somewhat reduced: from 2.35 kg/mm^2 to 2.06 kg/mm^2. The elongation at rupture is increased from 12.85 mm to 16.55 mm. The hardness of the leather is decreased from 378 kg to 314 kg. This points at an increase of the elastic properties of the skin after processing with urea.

The original photographs to be placed as figs. 1 and 2 were not received at the termination of editorial work due to postal delay. The plates will be delivered later.

Physico-mechanical properties of new parchment after different processing before aging
Duration of storage: 18 months

Table 2

Samples of new parchment processed	Directions	Average thickness in mm	Average breadth in mm	Average area of cross-section	Load at a tension of 1 kg/mm²	Elongation in mm at a tension of 1 kg/mm²	Load at rupture in kg	Elongation at rupture in mm	Limit of strength in kg/mm²	Module of elasticity in kg/cm²	Hardness in kg	Relative elongation in %
Control	Along	0.385	10.20	3.93	3.93	10.50	9.30	17.60	2.36	476	187	21.00
	Across	0.439	10.40	4.56	4.56	4.10	10.70	8.10	2.34	1 250	570	8.10
	Average	0.412	10.30	4.24	4.24	7.30	10.00	12.85	2.35	863	378	14.50
2% spermaceti emulsion	Along	0.418	10.00	4.18	4.18	8.83	6.80	14.30	1.62	556	232	17.66
	Across	0.433	10.40	4.50	4.50	5.60	11.20	11.90	2.48	909	409	11.20
	Average	0.425	10.20	4.34	4.34	7.21	9.00	13.10	2.05	732	320	14.42
10% alcohol solution of urea	Along	0.535	10.00	5.35	5.35	8.16	10.30	16.80	1.92	625	219	16.32
	Across	0.451	9.86	4.44	4.44	5.60	9.83	16.30	2.21	909	409	11.20
	Average	0.493	9.93	4.89	4.89	6.88	10.06	16.55	2.06	767	314	13.76
10% alcohol solution of urea + 2% spermaceti emulsion	Along	0.387	10.20	3.94	3.94	5.41	9.71	15.10	2.46	909	426	10.82
	Across	0.449	10.00	4.49	4.49	4.15	12.20	15.50	2.71	1 250	554	8.30
	Average	0.418	10.00	4.21	4.21	4.78	10.95	15.30	2.58	1 079	490	9.61

After artificial aging (see table 3) the strength and the hardness of new parchment is increased.

In table 4 are listed the data from physico-mechanical tests of old binding parchment before aging. After processing with urea, the strength is slightly decreased. The load at rupture in the control samples is equal to 29.20 kg, and in samples processed with urea 28.18 kg. The limit of strength is also slightly decreased, namely from 6.64 kg/mm² to 6.49 kg/mm². The elongation is increased from 10.78 mm to 12.07 mm, and the hardness is decreased from 2167 kg to 2072 kg.

After artifical aging (see table 5) the strength of old binding parchment is also slightly decreased. In the control samples the load at rupture was equal to 28.90 kg, and in samples processed with urea it was equal to 28 kg. The limit of strength is also reduced after processing: from 7.37 kg/mm² to 6.77 kg/mm². The elongation is increased from 9.90 mm to 12.30 mm. The hardness is almost doubly decreased: from 3352 kg to 1952 kg.

Particularly good results were obtained from the processing of old pigskin binding parchment with a 10% alcohol solution of urea (see table 6) – the load at rupture being increased from 16.17 kg to 18 kg. The limit of strength increased from 1.73 kg/mm² to 1.93 kg/mm², and elongation increased from 6.35 mm to 12.78 mm. The hardness decreased from 6933 kg to 3772 kg.

Table 7 gives the physico-chemical properties of old writing parchment (vellum). Processing with a 10% alcohol solution of urea somewhat decreases the strength of the parchment. The load at rupture of the control samples was 13.92 kg, and in samples processed with urea 11.85 kg. The limit of strength was reduced from 7.17 kg/mm² to 6.01 kg/mm². The lengthening at rupture after processing was increased from 6.05 mm to 7.35 mm. The hardness was reduced from 970 kg to 942 kg.

Particularly good results were obtained from the processing of writing parchment with a 10% alcohol solution of urea followed by greasing with a 2% spermaceti emulsion.

In this case, both the strength and the elasticity of the writing parchment were somewhat increased. Thus the load at rupture in the control samples was 13.92 kg, and after processing with urea it was increased to 15.59 kg. The limit of strength was increased from 7.17 kg/mm² to 8.20 kg/mm². The hardness is considerably reduced, namely from 970 kg to 767 kg.

Thus, facts from physico-mechanical testing of parchments processed with a 10% solution of urea, and with urea followed by greasing with a 2% spermaceti emulsion, indicate that urea and spermaceti have a bene-

Physico-mechanical properties of new parchment after artificial aging (10 hours' irradiation by a mercury quartz lamp of the type PRK-2). Duration of storage: 18 months

Table 3

Samples of new parchment processed	Directions	Average thickness in mm	Average breadth in mm	Cross-section in mm²	Load at a tension of 1 kg/mm²	Elongation in mm at a tension of 1 kg/mm²	Load at rupture in kg	Elongation at rupture in kg	Limit of strength in kg/mm²	Module of elasticity in kg/cm²	Hardness in kg	Relative elongation in mm
Control	Along	0.432	10.30	4.45	4.45	10.55	7.35	15.81	1.65	476	211	21.10
	Across	0.421	9.80	4.12	4.12	9.75	8.00	12.25	1.21	526	216	19.50
	Average	0.426	10.05	4.28	4.28	10.15	7.67	14.03	1.43	501	214	20.30
2% spermaceti emulsion	Along	0.432	9.83	4.24	4.24	6.90	7.90	14.00	1.86	714	302	13.80
	Across	0.441	10.00	4.41	4.41	7.10	8.82	15.00	2.00	714	314	14.20
	Average	0.436	9.91	4.32	4.32	7.00	8.36	14.50	1.93	714	308	14.00
10% alcohol solution of urea	Along	0.452	9.90	4.47	4.47	4.33	11.40	15.30	2.55	1 111	496	8.66
	Across	0.396	10.50	4.15	4.15	4.66	8.20	11.30	1.97	1 000	415	9.32
	Average	0.424	10.20	4.31	4.31	4.49	9.80	13.30	2.26	1 055	454	8.98
10% alcohol solution of urea + 2% spermaceti emulsion	Along	0.459	10.10	4.64	4.64	8.04	8.30	10.80	1.79	625	290	16.08
	Across	0.451	10.00	4.51	4.51	3.80	9.55	18.80	2.11	1 250	563	7.60
	Average	0.455	10.05	4.57	4.57	5.92	8.92	14.80	1.95	937	428	9.14

The physico-mechanical properties of old binding parchment (parchment of calfskin) after different processing. Duration of storage: 18 months — Table 4

Samples of binding parchment processed	Directions	Average thickness in mm	Average breadth in mm	Cross-section in mm²	Load at a tension of 1 kg/mm²	Elongation in mm at a tension of 1 kg/mm²	Load at rupture in kg	Elongation in mm	Limit of strength in kg/mm²	Module of elasticity in kg/cm²	Hardness in kg	Relative elongation in %
Control	Along	0.443	10.84	4.70	4.70	1.00	36.80	10.70	7.82	5 000	2 357	2.00
	Across	0.384	10.30	3.95	3.95	1.00	21.60	10.87	5.46	5 000	1 978	2.00
	Average	0.408	10.57	4.32	4.32	1.00	29.20	10.78	6.64	5 000	2 167	2.00
2% spermaceti emulsion	Along	0.437	11.00	4.80	4.80	1.00	38.03	13.60	7.92	5 000	2 403	2.00
	Across	0.368	10.96	4.04	4.04	1.00	23.08	13.50	5.71	5 000	2 019	2.00
	Average	0.402	10.98	4.42	4.42	1.00	31.05	13.55	6.81	5 000	2 211	2.00
10% alcohol solution of urea	Along	0.386	10.70	4.28	4.28	1.00	33.01	11.75	7.71	4 583	1 976	2.00
	Across	0.408	10.56	4.42	4.42	1.00	23.36	12.40	5.28	5 000	2 168	2.00
	Average	0.397	10.63	4.35	4.35	1.00	28.18	12.07	6.49	4 791	2 072	2.00

The physico-mechanical properties of old binding parchment (calfskin) after artificial aging (10 hours' irradiation by a mercury quartz lamp of the type PRK-2) — Table 5

Samples of binding parchment processed	Directions	Average thickness in mm	Average breadth in mm	Cross-section in mm²	Load at a tension of 1 kg/mm²	Elongation in mm at a tension of 1 kg/mm²	Load at rupture in kg	Elongation at rupture in mm	Limit of strength in kg/mm²	Module of elasticity in kg/cm²	Hardness in kg	Relative elongation in %
Control	Along	0.334	11.00	3.74	3.74	0.58	34.30	8.80	9.17	8 888	3 299	1.14
	Across	0.392	10.60	4.21	4.21	0.68	23.50	11.00	5.58	8 000	3 459	1.36
	Average	0.363	10.80	3.97	3.97	0.62	28.90	9.90	7.37	8 444	3 352	1.24
2% spermaceti emulsion	Along	0.402	10.20	4.09	4.09	1.00	35.50	11.70	8.68	5 000	2 045	2.00
	Across	0.369	10.50	3.91	3.91	1.00	22.10	14.00	5.65	5 000	1 955	2.00
	Average	0.385	10.35	4.00	4.00	1.00	28.80	12.85	7.16	5 000	2 000	2.00
10% alcohol solution of urea	Along	0.382	11.00	4.17	4.17	1.00	34.80	12.60	8.34	5 000	2 139	2.00
	Across	0.370	10.50	4.05	4.05	1.15	21.20	12.00	5.21	4 500	1 875	2.30
	Average	0.376	10.70	4.11	4.11	1.075	28.00	12.30	6.77	4 750	1 952	2.15

Physico-mechanical properties of old binding parchment (pigskin) after processing
Duration of storage: 18 months

Table 6

Samples of binding parchment processed	Directions	Average thickness in mm	Average breadth in mm	Cross-section in mm²	Load at a tension of 1 kg/mm²	Elongation in mm at a tension of 1 kg/mm²	Load at rupture in kg	Elongation at rupture in mm	Limit of strength in kg/mm²	Module of elasticity in kg/cm²	Hardness in kg	Relative elongation in %	Remarks
Control	Along	0.778	10.70	8.35	8.35	0.70	17.05	6.40	2.01	7916	6570	1.40	
	Across	0.892	10.60	9.45	9.45	0.82	15.30	6.30	1.46	7666	7571	1.64	
	Average	0.835	10.65	8.90	8.90	0.76	16.17	6.35	1.73	7791	6933	1.52	
10% alcohol solution of urea + a 2% spermaceti emulsion	Along	0.828	10.90	9.01	9.01	1.42	19.90	13.06	2.20	3736	3332	2.84	
	Across	0.838	11.44	9.59	9.59	1.20	16.10	12.50	1.67	4377	3951	2.40	
	Average	0.833	11.17	9.30	9.30	1.28	18.00	12.78	1.93	4056	3772	2.56	

Physico-mechanical properties of old writing parchment after processing
Duration of storage: 12 months

Table 7

Samples of writing parchment processed	Directions	Average thickness in mm	Average breadth in mm	Cross-section in mm²	Load at a tension of 1 kg/mm²	Elongation in mm at a tension of 1 kg/mm²	Load at rupture in kg	Elongation at rupture in mm	Limit of strength in kg/mm²	Module of elasticity in kg/cm²	Hardness in kg	Relative elongation in %	Remarks
Control	Along	0.183	10.33	1.88	1.88	1.00	11.25	6.33	5.96	5000	940	2.00	
	Across	0.191	10.53	2.00	2.00	1.00	16.60	5.77	8.24	5000	1000	2.00	
	Average	0.187	10.43	1.94	1.94	1.00	13.92	6.05	7.17	5000	970	2.00	
2% spermaceti emulsion	Along	0.187	10.18	1.90	1.90	1.50	9.30	7.91	4.86	5000	942	2.00	
	Across	0.186	10.84	1.86	1.86	1.00	16.16	6.41	8.54	3300	632	3.00	
	Average	0.186	10.51	1.88	1.88	1.25	12.74	7.16	6.70	4150	780	2.50	
10% alcohol solution of urea	Along	1.191	10.60	2.01	2.01	1.03	8.66	7.66	4.56	4850	989	2.00	
	Across	0.182	10.66	1.94	1.94	1.00	15.05	7.05	7.72	5000	896	2.00	
	Average	0.186	10.63	1.97	1.97	1.01	11.85	7.35	6.01	4925	972	2.00	
10% alcohol solution of urea + a 2% spermaceti emulsion	Along	0.179	10.50	1.88	1.88	1.33	16.15	11.00	7.74	5000	781	2.50	
	Across	0.169	10.64	1.83	1.83	1.00	15.04	7.81	8.66	3300	626	2.66	
	Average	0.174	10.57	1.85	1.85	1.16	15.59	9.40	8.20	4150	767	2.32	

ficial effect on old parchment. To examine the effect of urea on parchment Mr. G. R. Vol'pert, a scientific collaborator of the Central Scientific Institute of the Leather Industry, has carried out a systematic histological analysis of parchment processed with a 10% alcohol solution of urea. The histological analysis showed that the structure of collagen binding or viscosity becomes clearer after processing with urea, and the fibres swell to a certain extent.

Consequently, the signs of damage to the collagen fibres are lacking.

From the physico-chemical properties were determined: The active acidity (pH) of parchment before and after processing with urea the oxyproline amino acid, the presence of which indicates destruction of collagen, humidity of the parchment, hygroscopicity and emission of moisture from the parchment before and after processing with urea.

The acidity (pH) was determined potentiometrically (the potentiometer was an LP-5 with a glass electrode) with a pottasium chloride 0.1 N extract.

Processing with urea does not change the pH of the parchment and thus causes no damage to it. The pH of old binding parchment before and after processing is 7.25. The pH of old writing parchment (vellum) before and after processing is 7.15. The pH of new parchment before and after processing is 3.30. The pH of a 10% alcohol solution of urea is 7.25, and the pH of a 20% water solution of urea is 8.43.

In order to determine the oxyproline, we used the colorimetric method of Neuman and Logan which is based on the fact that products of oxidation of oxyproline of potassium peroxide give a red colouring[21] on interaction with dimethyl-benzaldehyde.

Tests of the oxyproline for all sorts of parchment after processing with a 10% alcohol solution of urea were negative.

We determined the oxyproline also from samples of parchment which had been processed with urea, and after processing had been subjected to ultra-violet rays (10 hours' irradiation with a mercury-quartz lamp of the type PRK-2). In this case the results were also negative. This points to the fact that processing with urea does not cause the destruction of the collagen into the amino acids.

The humidity, the hygroscopicity and the emission of moisture from differently processed parchments are of special interest. Table 8 gives facts about the humidity of non-processed and processed parchments at a relative humidity of the air of 57%, 67% and 82%.

The facts in this table indicate that the humidity of parchments processed with a 10% alcohol solution of urea, and a 10% solution of urea

Table 8

Humidity of differently processed parchments in %

Name of the process	Relative humidity of the air									
	Old binding parchment (calfskin)			Old writing parchment (vellum)			New parchment			
	57%	67%	82%	57%	67%	82%	57%	67%	82%	
Non-processed	11.02	15.89	16.33	11.72	16.48	19.15	9.24	12.84	14.58	
50% alcohol	—	14.46	—	—	13.28	—	—	9.82	—	
10% urea with 50% alcohol	8.92	12.46	13.75	8.50	13.70	19.16	7.45	12.41	14.19	
10% urea with 50% alcohol + a 2% spermaceti emulsion	8.50	15.70	15.51	7.60	13.71	18.57	8.90	15.44	15.69	
2% spermaceti emulsion (alcohol-benzene)	8.47	15.64	15.85	7.07	15.90	17.66	8.82	11.36	14.51	

followed by greasing with a 2 % spermaceti emulsion, is in all cases lower than the humidity of non-processed parchments, or slightly higher than the control samples processed with 50 % alcohol. Figures 3, 4 and 5 show curves of the hygroscopicity of differently processed parchments at 100 % at a temperature of 18–20° C, and under exsiccant conditions. From the curves in fig. 3 we see that the hygroscopicity of old binding parchment processed with a 10 % solution of urea in 50 % alcohol, when equilibrium sets in (24, 28 and 32 hours), is 1.75 % lower than the hygroscopicity of the control samples (parchment processed with 50 % alcohol) as compared with non-processed parchment. The hygroscopicity of old binding parchment processed with a 10 % alcohol solution of urea followed by greasing with a spermaceti emulsion, is more than 7–12 % greater. Processing with a spermaceti emulsion reduces the hygroscopicity of old binding parchment. The hygroscopicity of old writing parchment processed with a 10 % solution of urea in 50 % alcohol and urea followed by greasing with a spermaceti emulsion, is, when equilibrium is reached, 2–5 % greater than the hygroscopicity of the control samples (the curves in fig. 4).

The hygroscopicity after processing is increased 13–14 % as compared with non-processed parchment.

The hygroscopicity of new parchment (the curves in fig. 5) after processing with urea is, when equilibrium is reached, slightly greater than the hygroscopicity of the control samples (0.65 %). In this case, the hygroscopicity of non-processed samples is, when equilibrium is reached, greater than the hygroscopicity of the samples processed with urea, and greater than the samples processed with urea followed by greasing with spermaceti. The processing of new parchment with urea does not increase its hygroscopic properties.

It was thought interesting to observe how hygroscopicity of parchment is increased in connection with the processing under usual natural conditions. For this purpose we took samples of differently processed parchments after six months' storage in air. The hygroscopicity of these samples, which were suspended on special stands in an isolated room, was measured daily for 30–45 days. These results are given in the curves in figures 6, 7 and 8, and show that, under natural conditions, the hygroscopicity of old binding parchment and of new parchment after processing with urea is 0.2–0.4 % less than the hygroscopicity of the control samples, and of non-processed samples of parchment at a relative humidity of the air of 50 % and less.

At a relative humidity of the air of 55–75 % the hygroscopicity of processed samples is 0.5–1.5 % greater than that of the control samples. The

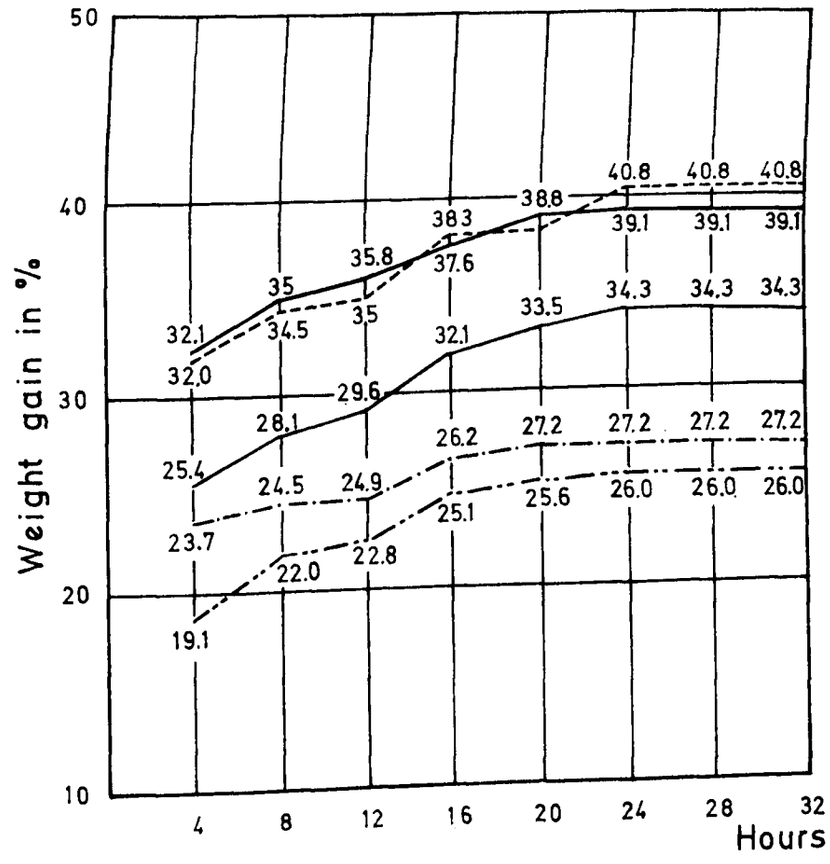

Fig. 3. *The hygroscopicity of old binding parchment at 100 % humidity*

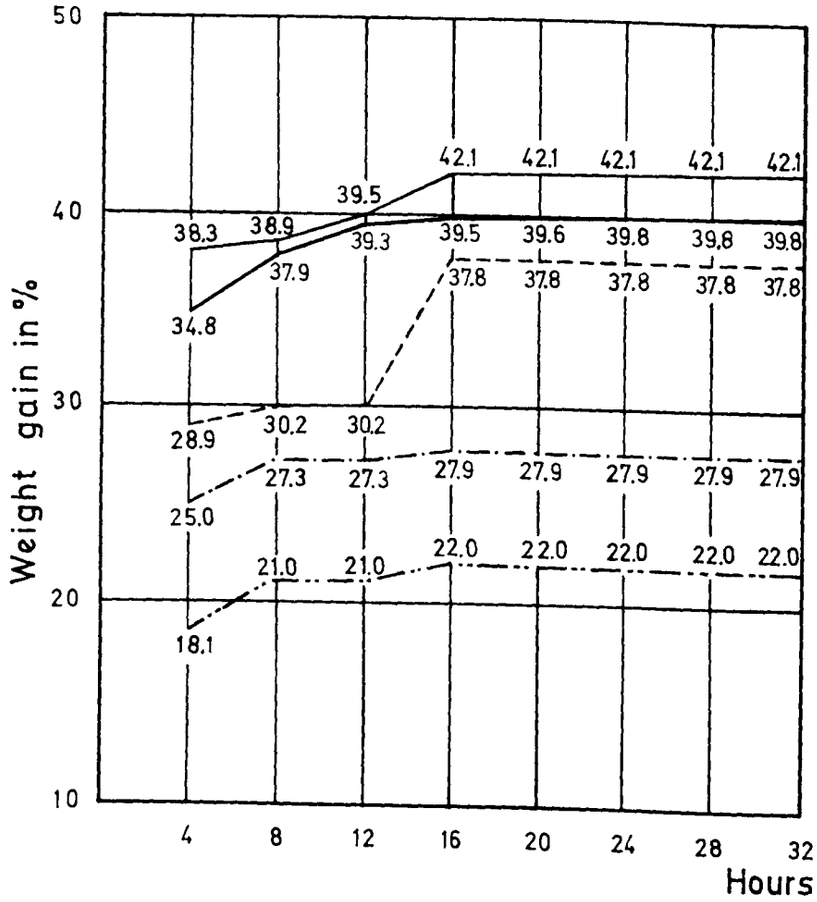

Fig. 4. *The hygroscopicity of old writing parchment at 100 % humidity*

2 % spermaceti
10 % urea
10 % urea + 2 % spermaceti
Non-processed
50 % alcohol

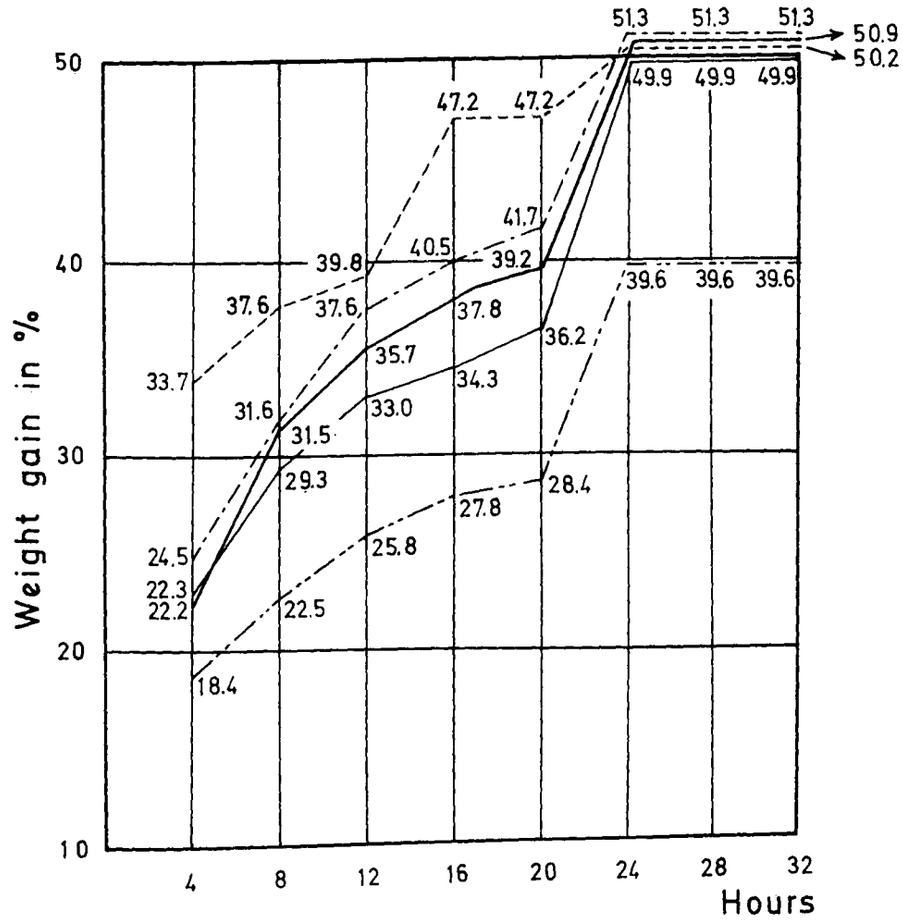

Fig. 5. *The hygroscopicity of new parchment at 100 % humidity*

2 % spermaceti
10 % urea
10 % urea + 2 % spermaceti
Non-processed
50 % alcohol

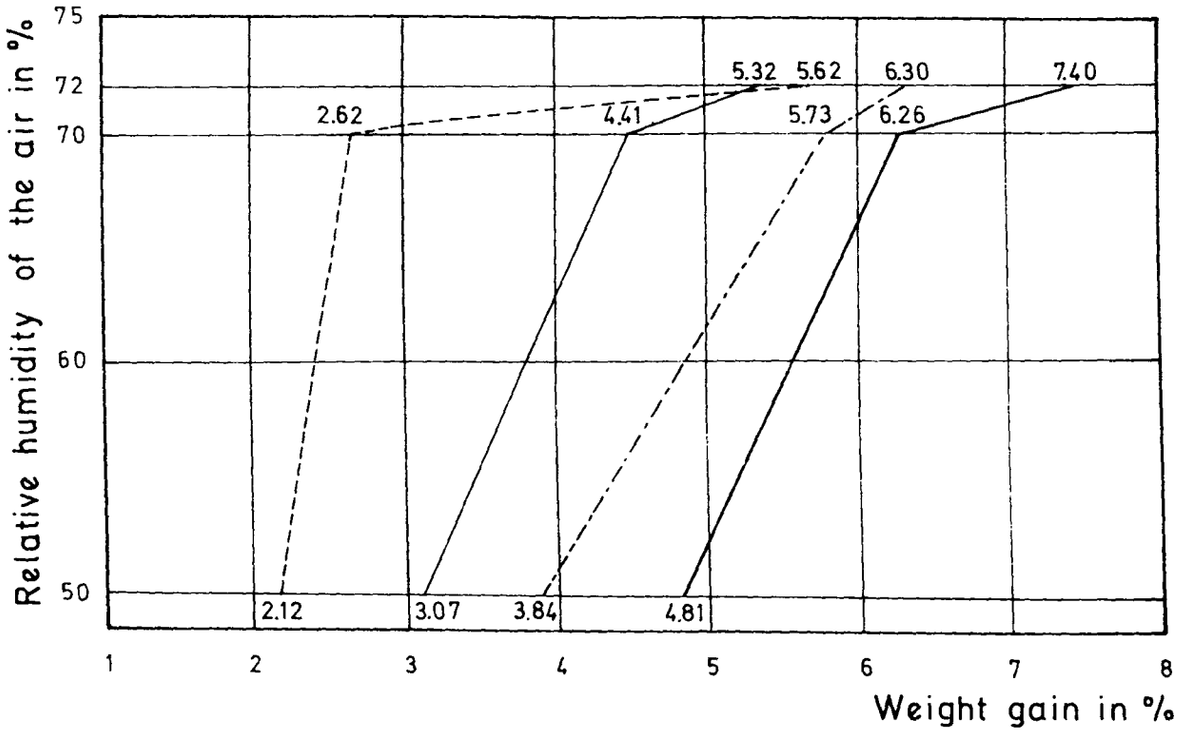

Fig. 7. *The hygroscopicity of old writing parchment under natural conditions 6 months after processing*

10% urea
10% urea + 2% spermaceti
Non-processed
50% alcohol

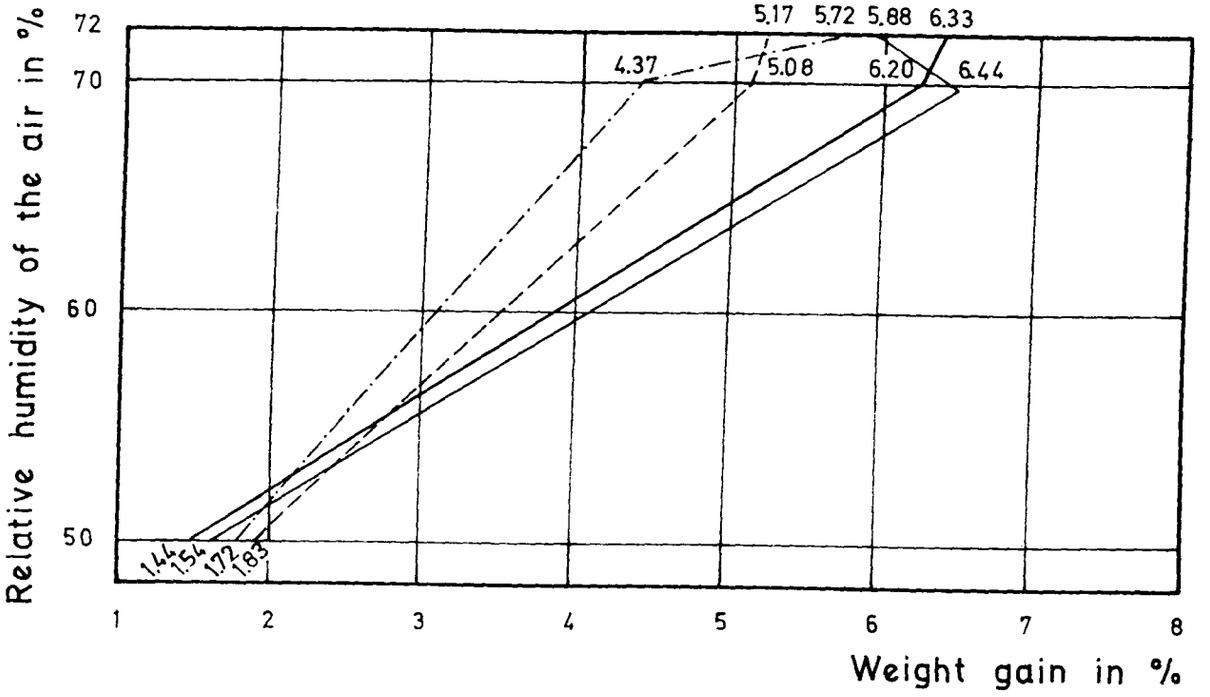

Fig. 6. *The hygroscopicity of old binding parchment under natural conditions 6 months and 2 weeks after processing*

10% urea
10% urea + 2% spermaceti
Non-processed
50% alcohol

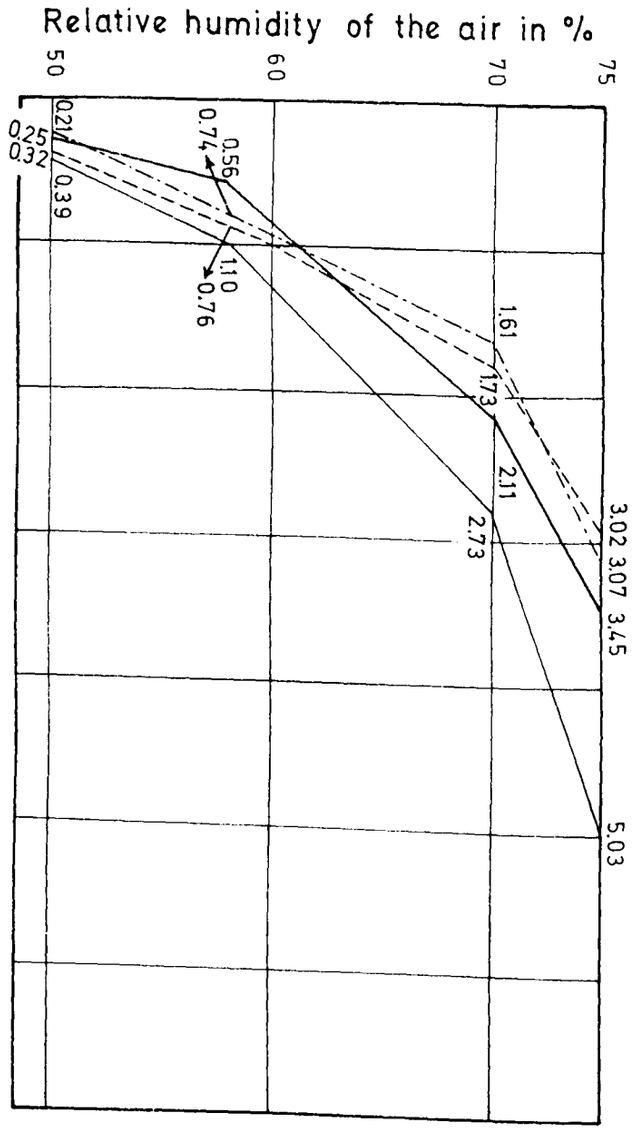

Fig. 8. The hygroscopicity of new parchment under natural conditions 6 months after processing

hygroscopicity of old writing parchment after processing with urea is 1–2.7 % greater than the hygroscopicity of the control samples and of non-processed samples.

Both at a low and at a high degree of relative air humidity, the hygroscopicity of writing parchment processed with 10 % urea followed by greasing with a 2 % spermaceti emulsion, is less than the hygroscopicity of non-processed parchment and on an average 2 % greater than the hygroscopicity of the control samples.

The determination of the emission of moisture showed that when a degree of equilibrium is reached the amount of moisture given off is equal to the moisture absorbed, and sometimes exceeds it. Thus, it appears from the above that the processing of parchment with a 10 % alcohol solution of urea and a following greasing of the parchment with a 2 % spermaceti emulsion, does not lead to an abrupt increase of the hygroscopicity of the parchment. A slight increase in the hygroscopicity of the parchment cannot cause damage to the parchment.

Of special importance when restoring manuscripts on parchment is the problem of fixing and restoring faded texts. For this purpose we studied the effect on the text of the substances used for the cleaning and softening of parchment. These substances are: Water, 96 % alcohol, 50 % alcohol, 2 % spermaceti emulsion, 20 % water solution of urea and 10 % alcohol solution of urea.

Testing was carried out with texts written in Iron Gallic Inks, Indian Ink, in printing colours, in the colours of engravings, in the colours of miniatures and in the colours of capital letters. Tests were performed as follows: Parchments with different texts and different colours were processed with the above-mentioned substances (30 minutes in a bath of the solution), whereafter the samples were put in press for 12 hours between sheets of filter-paper. The effect of a given substance on the text and the colours could then be evaluated.

These experiments confirmed our assumption that water and water solution destroy the text and the colours on parchment. Alcohol and alcohol solutions do not destroy the text and the colours on parchment, which is understandable. Very often old inks and colours contained plant gum as binding substances, and sometimes they contained fish glue or even sturgeon glue. The colours were very often smoothed out on egg yolk on the white of an egg. Gums, fish clay and white of egg are desposited by alcohol. Therefore processing of a text on parchment with 96 % alcohol does not destroy the text, on the contrary it strengthens it.

Some colours on miniatures and capital letters leave a slight trace on filter-paper even after processing with 96% alcohol, and therefore it is advisable to place parchment manuscripts in press after processing them with urea between sheets of paraffined paper.

Thus processing of texts with 96% alcohol and softening of parchment with 10% alcohol solution of urea and a 2% spermaceti emulsion do not neccessitate any special strengthening of the text.

The question of the restoration of faded texts on old manuscripts is very important. The Laboratory of Conservation and Restoration of Documents at the Academy of Sciences of the U.S.S.R. in Leningrad and the Main Archival Direction in Moscow are much concerned with these problems. To a wide extent they use the method of processing manuscripts with faded texts with ultra-violet and infra-red rays. However, nobody works with the restoration of faded texts on parchment. We had at our disposal a prayer book which had suffered damage during a fire when the text had been almost washed off by water. Knowing that tannin is a constituent of Iron Gallic Inks, tannin was tried for the restoration of the texts. For this purpose a water solution of tannin in concentrations from 2–6% was applied. The best results were obtained with a 4% solution of tannin. The text of this prayer book was succesfully restored.

After we had thus obtained experience, it was possible to restore the text of two 18th century manuscripts and an old Armenian text of a manuscript with coloured miniatures from the 10th century.

However, before undertaking the chemical restoration of a faded text, the manuscript must be photographed in ultra-violet light (tannin is not transparent to ultra-violet light) in order to ascertain that it is not a palimpsest, since when restoring a text by means of tannin, the underlying text may be lost.

On the basis of chemical, histological and physico-mechanical analysis, the following conclusions were reached:

1. A 10% alcohol solution of urea is the best agent for softening old, dried-out parchments and diminishing the deformation of sheets. In order to increase the strength and elasticity after using urea on the parchment, it should be processed with a 1–2% spermaceti emulsion.

2. Non-deformed, dried-out parchments must not be processed with urea. It is sufficient to soften such parchments – after a previous cleansing to remove dust and dirt – with a 1–2% spermaceti emulsion, dependent on the thickness of the leaves of the parchment.

3. The processing of parchment with a 10% alcohol solution of urea does not lead to an abrupt increase of the hygroscopic properties of the parchment. An insignificant increase (i.e. 0.5–1.5%) of the hygroscopicity under natural conditions cannot cause damage to the parchment, and conversely helps to preserve the elasticity of the parchment.

4. The text and many of the colours found on parchment manuscripts are not destroyed by the substances recommended for the softening and cleaning of parchments: 96% alcohol, 10% alcohol solution of urea and a 1–2% spermaceti emulsion.

5. Faded texts on parchment manuscripts may be restored with a 4% water solution, but it should first be ascertained whether the manuscript is a palimpsest.

Abstracts

Characteristics and aging processes of parchment are described and a critical review of some methods of softenings is given.

Research data in changings of parchment under the influence of alcohol solution of urea with a subsequent fatting by spermaceti emulsion are given. The method of softening and restoring of parchments is recommended.

Описаны свойства и процессы старения пергаментной кожи и дан критический обзор некоторых методов смягчения.

Приводятся данные исследования изменений пергаментной кожи под влиянием обработки спиртовым раствором мочевины с последующим жированием спермацетовой эмульсией.

Рекомендован метод смягчения и реставрации пергаментов.

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Instructions for the Softening of Parchment Manuscripts and Bookbindings

by I. K. BELAYA

When restoring parchment, the fundamental work consists of the softening and straightening of the dried-out, deformed and sometimes even cemented sheets, and the preservation of the text and the figures on the parchment.

I. *Preliminary Work*

1. A report on the state of the parchment, the fixing of the bulk, and the method of the work should be drawn up.

2. Documents or books of parchment should be photographed with the greatest possible detail before softening takes place.

3. Seals should be removed from documents, and a drawing made of the knotting of the string to which the seal was fastened, so that after softening the seal may be attached to the document in exactly the same way.

Remark: Seals should only be removed if they are inconvenient.

II. *Materials*

1. Two large sheets of glass, 50 × 60 cm
2. Hygroscopic cotton
3. Filter-paper
4. Paraffin paper
5. 96 % rectified alcohol
6. Distilled water
7. A 16 % alcohol solution of urea
8. A 2 % spermaceti emulsion
9. Chemically pure benzene
10. Phials holding 10 ml, 100 ml and 200 ml
11. Sheets of thick, smooth cardboard, 50 × 60 cm
12. Technical scales or druggists' scales
13. A press

III. *Preparatory Work*

Before softening the parchment, the following solutions should be prepared:

1. A solution of 50% alcohol: 106 mg of 96% alcohol diluted with water to 200 ml.

2. A 10% alcohol solution of urea: 10 g of urea should be weighed and dissolved in 100 ml of 50% alcohol.

3. A 20% spermaceti solution: 20 g of spermaceti should be weighed, poured into a phial with a ground glass stopper and dissolved in 100 ml chemically pure benzene.

4. A 2% spermaceti emulsion should be prepared: 10 ml of 20% spermaceti should be poured into benzene in a phial with a ground glass stopper. To this, 90 ml of 96% alcohol should be added while stirring continously. It should be firmly corked and shaken until a homogenous emulsion is obtained. Before use the emulsion should be stirred.

Remarks: 1. Work with benzene should take place in a fume hood.

2. For thin parchments, a 1% spermaceti emulsion (5 ml of 20% spermaceti and 95 ml of 96% alcohol) may be used.

5. The text and the colours of drawings should be tasted for any tendency to run. This should be carried out with 96% alcohol, 10% urea and 2% spermaceti emulsion. Testing should take place where the text and the figures are of less importance by rubbing on the solution with hygroscopic cotton. If there is any tendency to run, a chemical laboratory should fix the text and the colours.

IV. *The Softening of Deformed, Dried-out Parchment*

1. Parchments should be placed on a large sheet of glass, and the dirty sheets rubbed with a wad of cotton moistened with distilled water and thoroughly wrung out. Great care must be taken, and the text and the figures on the parchment should not be touched.

2. Immediately after cleaning with distilled water, the parchment should be processed with 96% alcohol. Processing with alcohol is necessary to fix the text, and to dry and clean the moistened parchment. The text and the whole sheet of parchment should be swiftly moistened using a wad of cotton.

3. If a manuscript consists of several sheets, ensuing sheets should only be moistened when the preceding sheet has been processed with 96% alcohol, otherwise the moistened sheet will be distorted since parchment is easily distorted by moisture.

4. After processing with alcohol, the parchment should be lavishly moistened with a 10% solution of urea using wad of cotton.

5. When parchments are very deformed and brittle, they should be placed in a large drain and a 10% solution of urea poured over them every 30 minutes.

Subsequently the parchment should be put in press, sheet by sheet, for 24 hours between sheets of paraffin-paper and thick, smooth cardboard.

When the parchment is removed from the press, it should be processed with a 2% spermaceti emulsion. The entire surface of each sheet should be swiftly moistened with a wad of cotton, thereafter each sheet is pressed for a further 24 hours or more between sheets of paraffin-paper and cardboard.

After removal, the sheets should be put between sheets of filter-paper, and then placed between large sheets of glass and remain under light pressure until the spermaceti has completely penetrated into the parchment. After 7–10 days the parchment is absolutely dry.

V. *The Softening of Undeformed, Dried-out Parchment*

Parchment which is dried-out but not deformed may be processed with a 10% solution of urea in the following manner:

1. Cleaning with a moistened wad of cotton as mentoined above.

2. Processing with 96% alcohol.

3. Processing with a 1% or 2% spermaceti emulsion and pressing for 24 hours or more between sheets of paraffin-paper and sheets of smooth, thick cardboard.

4. After pressing, the parchment sheets should be placed between sheets of filter-paper between large sheets of glass and remain under light pressure for 7–10 days, until the spermaceti has completely penetrated into the parchment, and it is completely dry.

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Paper Cleaning

by PAUL N. BANKS

Dry Cleaning Methods

The dry methods of cleaning paper are, for the most part, so simple and obvious that I will not dwell on them long. The most basic method of cleaning paper is dusting; I have found that there are several Japanese brushes available which are gentle and effective. In the Extra Bindery at Donnelley's compressed air is considered essential; in the National Archives in Washington[1] and the Detroit Public Library[2] air hoses are used in conjunction with exhaust chambers which draw out the loosened dirt.

There are a number of types of erasers available: kneaded, soap, art gum, Pink Pearl, vinyl and others. These types are nearly or entirely non-abrasive. The kneaded eraser is probably the most gentle; it has a slightly adhesive quality which enables it to be used with almost a blotting action. Vinyl erasers (the »Magic-Rub« brand is available in pencil form as well as the conventional cubic form) are extremely gentle, and have the quality of tending to pick up their own crumbs, so that they are less messy to use.

A word of caution may be in order about vinyl erasers. Vinyl resins are peculiar materials; they have the ability to dissolve many other resins. We cannot use vinyl-coated bookbinding fabrics because books so bound would stick to all of the ones already bound in pyroxylin cloth, and I have a gooey, bright yellow mess in the drawer of my workbench which was caused by the contact of a vinyl eraser with several common wooden pencils. Although there is probably no danger from using vinyl erasers on printed materials, it might be advisable to be especially cautious about removing all crumbs.

Fresh bread has long been advocated as an efficient means for cleaning surface dust from paper; I must confess that I have never tried it. But I have observed that a loaf of bread left in a paper bag will stain it with grease. My feeling is that the various devices which are meant specifically for cleaning paper are probably adequate.

A new material which has been used for cleaning paper is Absorene wallpaper cleaner, a pink, dough-like substance sold in one-pound cans in paint and hardware stores. There are also other, similar brands available.

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It is similar in its use and its effect to the kneaded eraser, but it is a great deal cheaper and is suitable for very large or very dusty surfaces. The best use that I have found for it is for cleaning the paper covering of books, slipcases, portfolios and the like.

Extremely useful gadgets for removing loose dust and dirt are the Opaline dry cleaning bags and similar devices. These consist of mesh bags which contain a substance which appears to be rubber or soap eraser dust; the bag is simply rubbed gently over the surface to be cleaned. When the surface of the bag is dirty from use, it may be twisted and the dirty particles fall away, leaving a clean surface to work with. Although the action of these pads is not as strong as that of actual erasers, they are effective in removing heavy films of loose dust from paper objects. They are sold in art supply stores.

The basic technique for using any type of erasing device is to hold the sheet being cleaned in the center and move the eraser from the center out to the edges. To use any other motion is to court disaster from tearing the sheet. It is, I believe, absolutely essential to remove all traces of crumbs from the objects being cleaned, as the crumbs are almost surely destructive. This is especially true of the Absorene wallpaper cleaner; its crumbs have a strong adhesive quality which makes them cling tenaciously if they dry on a sheet of paper. The material is water soluble, however, which gives an easy method of removing any crumbs which have become dried.

Some of us have wondered whether any of these erasing-type devices would leave any harmful residues in the paper, even when all visible traces were removed. In order to find out, the Library Technology Program of the American Library Association, in connection with its series of manuals on The Conservation of Library Materials, commissioned McCrone Associates to study these materials. The results, based on microscopic examination and accelerated aging tests of paper cleaned with them, seem to indicate that the common erasers, the Opaline bags and Absorene Wallpaper Cleaner are safe to use on paper. The detailed procedures and results of the tests have not, unfortunately, been published, although they are referred to in Carolyn Horton's *Cleaning and Preserving Bindings and Related Materials*, the first manual in LTP's series.[3]

One other experience that I have had, might be classed under dry cleaning methods. I was recently given a bound manuscript to work on which had two leaves stuck together by a thick, hard, dark mass, which might have been a disintegrated rubber band or chewing gum. I discovered that the material was thermoplastic, so I separated the pages and cleaned off the

worst of the incrustation by holding the pages over an upturned iron set at a very low heat. Most of the rest of the deposit was removed with solvents.

Solvent Methods of Cleaning Paper

Since the main use of solvents in connection with paper is to remove foreign matter which has usually penetrated into the texture of the paper, the key to their use is to either lay the sheet to be treated on absorbent material so that the foreign matter is drawn out with solvent before it can evaporate, or, in some cases, the use of a bath of the solvent where the foreign matter is so diluted that it can be said to be removed. If solvent is applied to a stain and simply allowed to evaporate, the stain will just be redistributed. In the case of thick deposits to be removed, the best principle is usually to soften the incrustation with solvent, remove it mechanically, and then remove the final traces as described above.

The solvents that I have found most useful are hexane, toluene, acetone, dimethyl formamide and pyridine. Note: All of these solvents are highly flammable, and all are moderately to highly toxic. Great care must be taken to avoid breathing the vapors, and pyridine and dimethyl formamide are absorbed through the skin.

Hexane and toluene seem to be effective for many kinds of grease, oil and wax stains. A mixture of the two solvents is often effective in removing deteriorated pressure-sensitive tapes. Acetone is, of course, effective for many types of lacquers, plastics and spirit varnishes. Denatured ethyl alcohol (methylated spirit) is also sometimes effective for the latter, if it has not oxidized too far. Dimethyl formamide and pyridine are effective for oxidized fats, oils and resins, but they are very drastic and very toxic.

Chlorinated solvents, such as perchlorethylene and trichlorethylene, which are widely used in the dry cleaning industry, and carbon tetrachloride, have been proposed, but there is some question as to their inocuousness for paper because of their chlorine content. Chlorinated solvents tend to be quite toxic, and carbon tetrachloride is highly so. Plenderleith[4] recommends petrol for wax and grease stains; it is apparently difficult to find white gasoline in this country now which does not have additives of unknown effect on paper; in addition, the lead compounds in most gasoline are toxic. Naptha, petroleum benzine or hexane will probably serve just as well.

I recently encountered an engraved opera score which had been heavily

marked with ball point pen. Bleaches seemed to affect the ball point ink almost not at all, but I discovered that dimethyl formamide dissolved the binder to such an extent that virtually all of the stain could be removed by placing the sheet face down on a blotter and soaking the verso with the solvent on a cotton swab. After each application, the spot being treated was moved to a clean spot on the blotter. This strong solvent softened the engraving ink, so that it had to be applied by tapping or rolling the swab rather than rubbing it.

Plenderleith[5] has also recommended dilute ammonia water for removing old spirit varnish if alcohol is not effective and Gettens[6] has successfully removed some resinous matter from paper with an aqueous solution of morpholine (which, like pyridine, in addition to being a solvent, has an alkaline reaction in water).

A very large number of solvents is available, and within the last decade or so, there has been some literature which permits solvents to be selected rationally for a specific problem, particularly where the exact nature of the substance to dissolved is known.[7,8] Solubility parameter and hydrogen bonding capacity of the solvent and solute must be matched, and then, within this framework, there may be a choice of solvents with different rates of evaporation, which will make the use of the solvent or mixture of solvents easier in the circumstances at hand. A scheme could be devised, based on these factors in the choice of a solvent for a particular job (as well as other factors such as toxicity or viscosity) which would permit one to choose a solvent systematically rather than on a hit-or-miss basis.

Wet Cleaning Methods Other Than Bleaching

Water has been called the universal solvent; that is, of course, an overstatement of the case, but it certainly does have some useful qualities. Washing old paper in plain water usually removes dark, soluble matter from it, often reduces waterstaining, removes some free acid from the paper, and permits wrinkles and other distorations to be pressed out. Pure water does something else good to many old papers: it increases their physical strength. This is apparently caused by the re-establishment of some of the broken hydrogen bonds in the cellulose molecule.[9]

Where any form of wet treatment is proposed, it should be remembered that water has a tendency to »set« surface dust, so that the latter should be removed by erasing before the object is immersed.

Some of the older books on bookbinding recommend a hot alum bath for removing waterstains from paper and »firming« it. In light of what Barrow[10] and others have said about the harmful effect of alum on paper, I would conclude that this treatment should be avoided. If »firming« of paper is needed, it can be achieved by adding sizing.

Soap has often been recommended for removing mud and general grime from paper; there is probably a place for this treatment. However, although soap is a specific chemical compound, the specification for soap which can be safely used on paper is as vague as »good quality« or »castille«. I am reluctant to use soap without knowing more about what to use. Non-ionic wetting agents such as Lissapol, Nonex and Tergitol Penetrant No. 7 have been recommended[11,12] and it appears that they are safe.

A badger shaving brush is an excellent tool for applying very gentle friction to a sheet of paper being treated with soap or wetting agent.

Enzymes are complex organic substances which, in their pure forms, catalyze the breakdown of specific organic substances into water-soluble products. For example, collagenase breaks down animal glue, whose principal constituent is the protein collagen, so that it can be easily rinsed away with water. Similarly, amylase digests starches. Laundries use commercial preparations of enzyme mixtures for removing difficult stains, usually those of a proteinaceous nature, and taka-diastase, which I believe is a mixture of enzymes, and which is sold in pharmacies for medicinal use, has been recommended for removing certain adhesive stains from paper. However, enzymes are usually effective only under very rigidly controlled conditions of temperature, water purity and pH, so that their use on a routine basis may never be practical. (They must also generally be bought fresh and stored under refrigeration to preserve their activity.)[13] Their main potential use, it seems to me, is in removing difficult residues of starch adhesives from paper. As older western papers are conventionally sized with glue or gelatine, an enzyme which would remove old glue from a piece of paper which had been used in a binding, for example, would also remove the sizing. More work needs to be done on the application of these interesting substances to paper conservation.

In the case of any chemical treatment to paper, thorough washing in running water is highly advisable to remove any traces of compounds which might later cause injury to the cellulose of the paper.

Two words of warning may be in order about any form of wet treatment for a paper object. In all cases where prints or drawings on paper are being handled, and in the case of many book pages, the sheets being so treated

should be supported while wet by means of a glass, plastic or paper sheet. The support can be put in the bottom of the tray before the sheet is immersed, or slid in when it is ready to be removed. Where books are being treated in their entirety, it is often impractical to support each sheet, and in many cases, the smaller sheets will support themselves adequately if handled carefully (they should always be slid, edgewise, out of the solution, so that the weight of the solution itself does not tear the sheet). But if the book is exceptionally valuable or if the sheets are unusually large or fragile, then even here they should be supported.

The other warning is about pressing. Bookbinders have probably been more at fault than print restorers in their insistence on over-pressing washed or bleached books. Early printing was done on crude presses with uneven types, so that much or all of the printed image was punched through the paper. In addition, most early letterpress printing was done on dampened paper, and the combination of the punch of the type and the uneven drying of the dampened paper caused a good deal of distortion in the leaves of the book. If, after a book has been given some form of wet treatment, it is pressed hard, all of this distortion is pressed out of the sheets, and it winds up looking like a bad facsimile. The same would, of course, hold true for etchings or engravings which have plate marks which should be preserved. Drying with blotters is the best method, with only enough pressure to ensure the required degree of flatness. Changing the blotters for dry ones at intervals during the drying process is advisable also, as it hastens drying and helps to prevent unwanted distortion. Even where punch is not a factor, changing blotters, with the consequent periodic release of pressure on the sheets, is desirable, to allow the paper to contract more-or-less naturally as it dries.

Bleaching Paper

There seem to be four major categories of methods for bleaching stains from paper widely employed at present. These are: chloramine-T, hypochlorites, sodium chlorite-chlorine dioxide, and potassium permanganate.

The use of chloramine-T was proposed in 1937 by Harold J. Plenderleith in *The Conservation of Prints and Drawings*.[14] The main advantages claimed for it were that it was very mild in its action, and that no destructive residues were left in the paper, so that it did not need to be rinsed from the treated sheet, although I believe that the implication even

then was that it would be preferable to rinse the sheet. I am aware of no contradiction of the idea that a 2 % solution of chloramine-T is not damaging to paper, but Harold Tribolet has observed that the dried residue of the bleach remains active and will bleach adjacent sheets of paper. This effect was observed when an endlining of colored paper was added to a book in a position adjacent to a leaf which had been treated with chloramine-T and not subsequently rinsed. In addition, there has finally been a published statement from the British Museum laboratory, albeit a highly obscure one, which indicates that chloramine-T *should* be rinsed from the treated sheet.[15]

I believe that chloramine-T is rightly considered to be the usual first step in attempting to bleach most stains from paper.

Bleaching paper with hypochlorites originated in the beginning of the nineteenth century, with the advent of bleaching powder or chloride of lime, which is calcium hypochlorite. Sodium hypochlorite is now customarily used because of its greater convenience. The latter is also known as chlorinated soda or eau de javelle.

Sheldon Keck has given, in *Technical Studies in the Field of Fine Arts* in 1936,[16] a method for bleaching prints with sodium hypochlorite which is very carefully worked out and described in detail. His procedures would seem to be desirable for operators who are not trained in chemistry, as he gives simple and apparently effective means for controlling the operation at each step, thus giving the operator some confidence that he is not unduly damaging the paper. It is not possible to give a detailed description of the process here, but briefly, it consists of bleaching the print in a bath containing 5.5 % of a 5 % sodium hypochlorite solution and 1/2 % concentrated hydrochloric acid, completing the bleaching in a bath of 1/2 ml of concentrated hydrochloric acid in 2700 mls of water, and neutralizing the acid with a bath of 2 mls concentrated ammonium hydroxide in 9 l of water. The sheet of paper to be bleached is placed in the three solutions in succession, the times depending on the circumstances.

The method given by Plenderleith[17] and others involves a stronger bleaching solution, made up of 5 % of a 10 % sodium hypochlorite solution, but no hydrochloric acid is added to the bleaching bath. If the paper is softened by the action of this solution, it can be somewhat mitigated by immersing the paper in a solution of »a teaspoonful of concentrated hydrochloric acid in a quart of water«, according to Plenderleith. A 2 % solution of photographer's hypo, sodium thiosulfate, completes the process by acting as an antichlor to remove the residual chlorine.

I am not able to evaluate the relative merits of the two sodium hypochlorite methods cited here, except for the greater controls offered by the Keck method.

In 1951 R. J. Gettens read a highly significant paper to the American Association of Museums annual meeting in Philadelphia, which was published the following year in expanded form in Museum.[18] This paper, entitled »*The bleaching of stained and discolored pictures on paper with sodium chlorite and chlorine dioxide*«, presented an entirely new and apparently safe method for bleaching prints, drawings and book pages. This method – actually three methods – is based on the bleaching action of chlorine dioxide gas, which is relatively easily generated from a solution of sodium chlorite. The process, based on one becoming widely used commercially for bleaching paper pulp among other things, does have one drawback for most conservators in that it requires equipment not usually found in the smaller conservation laboratory.

I will describe briefly the three techniques which Mr. Gettens proposes, all of which require a fume hood because of the disagreeable and somewhat toxic qualities of chlorine dioxide gas.

The first technique is the simplest, as it requires no special equipment other than the fume hood. A solution of sodium chlorite is made, to which is added formaldehyde, which releases the chlorine dioxine gas. A wetting agent is also added to the solution. The sheet to be bleached is placed in the bath for a period of fifteen minutes to an hour or more, as required to bleach the stain. It is then rinsed in running water for at least fifteen minutes to remove any residual sodium salts. The process is claimed not to make the paper staring white as some others do.

The second method proposed involves the use of an aqueous solution of chlorine dioxide: its advantage is that it can be used where only a minimum amount of immersion is desirable for the print or drawing. Chlorine dioxide gas is made in a special gas generator by dropping sulfuric acid into a solution of sodium chlorite. The gas is bubbled through water, where it goes into solution. The object, supported as usual on a sheet of glass or plastic, is immersed in the solution for the requisite amount of time. Mr. Gettens says that although at least a brief rinsing in plain water is desirable, it is not necessary in this case, as the chlorine dioxide is the only chemical left in the paper, and it is completely volatile.

For prints which cannot stand immersion at all, a third method is proposed. Chlorine dioxide gas is generated as in method II, but instead of being used as a solution in water, it is passed directly over the slightly

dampened print in a special sealed chamber. The chamber and the recommended fume hood both have glass windows, so that the progress of the bleaching can be followed. This method is recommended only where neither of the other two is applicable, as the oxidized end-products of the stains are left in the paper, and could revert to their original color in time.

The process involving potassium permanganate, which oxidizes many kinds of stains and converts them to brown manganese oxides, which can in turn be reduced by some other reagent to colorless and soluble substances which are then washed out of the paper, was first used around the turn of this century. The process is relatively simple: the sheet to be bleached is immersed for about five minutes in an aqueous solution of potassium permanganate of 0.5 % to 5 % concentration (depending on which recipe you read), then the sheet is placed in a bath of one of a number of solutions to reduce the resultant brown stain.

The earliest second bath which I am aware of is a solution of sulfurous acid. Potassium metabisulfite was apparently in use in the thirties, and oxalic acid was mentioned by Plenderleith in 1937. Other solutions proposed have been those of sodium sulfite, sodium hydrosulfite, and citric acid. All of these substances are apparently effective: the choice has been based on the question of damage to the paper. Unfortunately, most of what has been said so far about destructiveness or lack of it seems to have been based on theoretical considerations at best, or at worst, pure folklore. But a very interesting publication has come from Russia which may shed some light on the question.

R. R. Yabrova of the Department for Book Preservation and Restoration of the Lenin Library in Moscow published an article which was made available in English in 1964 by the Office of Technical Services in Washington,[19] which deals with the removal of dyes from paper. In setting out to find the most effective treatment, they decided upon the »well-known and widely used« potassium permanganate and oxalic acid process. Having established that it is effective for most kinds of stains, they then tried to find out, by objective means, its effect on paper.

Their recommended process involves the addition of a small amount of orthophosphoric acid to the permanganate solution, as the latter is more active in an acid medium. It was determined from the literature and checked in their laboratory that the phosphoric acid, in the concentrations recommended, is not harmful to paper. Unfortunately, they did not check the effect of sulfurous acid solution for the second bath, which is apparently as widely known as oxalic acid, but they did test oxalic acid and potassium

metabisulfite in their laboratory, and both were found to reduce the physical strength of the paper; the oxalic acid drastically so. It apparently should not be used on paper under any circumstances. The treatment for reducing the manganese oxides stains which the Russian workers found to be non-damaging to paper consists of a bath of 5 % sodium hydrosulfite (not to be confused with sodium hyposulfite). The paper is finally washed in plain water, then treated with water to which a small amount of ammonia has been added, then finally washed in water again.

Unfortunately it is not possible here to go into one important aspect of cleaning paper, i. e., media, and the related one of protecting certain images when the rest of the sheet is to be bleached. However, I would like to mention two specific points which may be of interest.

The customary procedure for protecting a signature written on a book page which is to be bleached, for example, is to paint over the writing with a solution of cellulose acetate or nitrate in the appropriate solvent. After the bleaching has been carried out, the protective material is removed with more of the same solvent. In the edition of Lydenberg and Archer's *The Care and Repair of Books* which was revised by John Alden,[20] an alternative method is proposed which is convenient, and perhaps also more effective. Alden suggests citting a small piece of cellulose acetate film to the required size, laying it over the area to be protected, and patting it with cotton dampened with acetone to seal it to the paper. This also can be removed after bleaching by the use of acetone.

When the Russian scientists started their work on bleaching paper, they were apparently mainly interested in bleaching ink stains of various kinds. Thus they started their work by attempting to find convenient means of identifying the dyes which are used in various writting and stamp-pad inks, to help them to select the most effective bleaching process. The first and more complete table given in the article shows the effect of eight reagents which can be used as spot tests on the nine dyes selected for testing; most of the reagents however do not give conclusive results. But they reduced the table to one showing the reactions to one of two reagents, a stannous chloride and hydrochloric acid solution, or 10 % hydrochloric acid, which, between them, will differentiate among all of the dyestuffs considered. Although the frame of reference is somewhat limited, and I believe that most workers would simply start by trying chloramine-T and, if that was not effective, one of the stronger processes, this table might be of use in certain situations.

As I have indicated, there has been a great deal of controversy over

the relative safety to cellulose of hypochlorites and of the permanganate process. Of the sources that I have seen, Douglas Cockerell,[21] the English binder of earlier in this century, and W. H. Langwell,[22] British chemist who is interested in paper, say, respectively, that the permanganate process is the safest bleaching method, and that it is certainly safer than hypochlorites. On the other hand, Sydney Cockerell,[23] Douglas' son and a well-known binder and restorer, and John Alden, in his recent revision of Lydenberg and Archer,[24] say that permanganate is to be used only as a last resort, and that fortunately the permanganate method has given way to safer methods, among them hypochlorites.

I believe that some of the controversy can be cleared up by citing again two of the workers whose writtings have already been mentioned.

Gettens, in trying to establish in fact the already theoretically established safety of chlorine dioxide, did some testing, which he describes as being somewhat crude, but which nevertheless gave some interesting results. Samples of filter paper, a nearly chemically pure cellulose, were placed for a period on eight months in atmospheres of chlorine and chlorine dioxide. In three weeks' time, there was palpable reduction in the tear-strength of those in the chlorine chamber, and none for those in the chlorine dioxide atmosphere; at the end of the eight months' period, the samples treated with chlorine dioxide still showed no detectable degradation, while those which had been in chlorine shattered at touch. In another series of tests, Gettens and his people bleached a variety of papers with hypochlorite and chlorine dioxide bleaches. Some were rinsed with plain water after bleaching; some specimens were artifically aged; others were exposed to daylight for several months. None of the specimens tested showed any evidence of degradation, as measured by the Elmendorf tear-resistance test, except one. This one was some French paper dated 1828 which had been bleached with sodium hypochlorite, rinsed in water, dried, and aged at 75° C. for seven days. This specimen gave »much lower« tear resistence values than any other sample tested.

The Russian workers also tested the effect of hypochlorite bleaches on paper. Their results showed an immediate, drastic drop in the folding strength of papers bleached with calcium hypochlorite solution, although there was little difference between the relative folding strength of bleached and unbleached samples after either natural or artificial aging. On the basis of the latter fact, i. e., that aged samples of bleached papers did not show significantly lower fold values than unbleached samples similarly aged, Yabrova contends that hypochlorites may be safely used for bleaching

stains where the recommended permanganate treatment fails. However, I would like to take issue with this. First, it is known that with old paper, at least, soaking in plain water often increases the physical strength, as I have pointed out, although this presumably is not true of new paper. It could be, then, that the initial drop in fold values is even more drastic than it appears. Moreover, there was *some* further decrease in folding strength values between the eight-month and eleven-month checks, and that the values for bleached papers are somewhat lower, admittedly not a great deal, than those of the unbleached papers, after accelerated aging. If we accept the contention of Barrow and others that three days' heat aging at 100° C. is roughly equivalent to 25 years of natural aging under average conditions, we can see that this accelerated aging of five days at 68° C. is not very drastic.

There are theoretical reasons, also, for believing that hypochlorites may degrade cellulose. Gettens gives us a graph, showing that under neutral conditions, hypochlorites have an oxidation potential approaching twice that of sodium chlorite, for example.

It must be stated, however, in defense of hypochlorites, that Yabrova states that the method may be used safely, although it seems to me that the evidence controverts this, and that Gettens says that he knows of no actual instances of damage to prints from bleaching with hypochlorites, despite theoretical objections to their use.

As I have stated, Yabrova seems to assume that potassium permanganate itself does no harm to cellulose, but that the reducing medium used after the permanganate solution, to remove the manganese oxides and excess permanganate, can indeed be harmful, depending on the compound used. She has shown that the permanganate method, when used with a five percent solution of sodium hydrosulfite, is quite safe for bleaching works of art or books on paper.

Thus I would make following tentative recommendations, based, I remind you, on what I have been able to glean from the literature, not on my knowledge of chemistry or on my limited experience with actual bleaching of paper.

1. Chloramine-T seems to be the least drastic and most conventient bleaching compound; it should probably be tried first.
2. If it is not effective, one of the sodium chlorite-chlorine dioxide methods should be employed if the requisite fume hood and other equipment are available.

3. That potassium permanganate-sodium hydrosulfite method be employed where a fume hood is not available.
4. That because of the evidence that hypochlorites may degrade cellulose, their use be avoided except in unusual cases.
5. That thorough washing in running water be used after all bleaching operations unless it is patently impossible to do so. I have heard the rule-of-thumb given that after a sheet of paper has been treated with chemicals, it should be washed for three times the period that it was exposed to the chemicals.

Since the original preparation of this article, some work of Mme. Flieder of Paris has come to my attention.[25] Some of her conclusions seem to contradict those of other recent literature. However, she tended to test the effect on paper of only those bleaching methods which were effective for her prepared stained samples, all of which consisted of intense fungal stains. Thus some milder treatments, which are effective for other kinds of stains, were not subjected to rigorous testing. It is in some respects difficult to interpret her data for the stronger bleaching treatments, in that the methods tested were selected uncritically from the literature that she found, and thus there are many similar tests in each group. I am not able to deduce which of the group of modern papers she discusses in the beginning of the article she finally made the tests on. It is striking that her conclusions about hypochlorites vis-à-vis permanganate and chlorine dioxide are the opposite of those of Yabrova and Gettens, respectively.

It is quite clear that a carefully planned, extensive program of testing the effects of bleaches on paper is needed, and it should be executed, if at all possible, on various kinds of old as well as new paper. It would perhaps be ideal if it were sponsored on an international scale, so that the thinking of many countries could be taken into account. In order to limit the amount of effort involved in such a program and to make the results clearer, the question of efficacy might be avoided, leaving to the individual conservator or another program the bases for choosing a safe bleaching procedure for the problem at hand.

Abstracts

Dry methods of cleaning paper, including air cleaning, brushing and erasing, are first discussed. A range of solvents is suggested, with discussion of their use and of recent theories of solvent activity. Cleaning with water, soap, detergents and enzymes is discussed, with warnings about safe handling of the object and about over-pressing. Finally, the various categories of bleaching are cited, including chloramine-T, hypochlorites, sodium chlorite-chlorine dioxide, and permanganate. The contradictory claims in the scientific literature for safety of various bleaches are cited, with a plea for a carefully planned testing program on the effects of bleaches on paper.

Впервые обсуждаются сухие методы очистки бумаги, включающие воздушную очистку, очистку щеткой, соскабливанием (стиранием). Предлагаются ряд растворителей с обсуждением их применения и новые теории растворяющего действия. При очистке водой, мылом, моющими веществами и энзимами необходимо осторожное обращение с предметом, без чрезмерного давления. В заключение приводятся различные классы отбеливателей, включающие хлорамин-Т, гипохлориты, хлорит натрия – двуокись хлора, перманганат. Приводятся противоречивые сведения из научной литературы о безопасности действия различных отбеливателей со ссылкой на тщательно проведенные испытания по влиянию отбеливателей на бумагу.

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Editor's note: Mr. Banks' article was one of six papers on »Paper: Composition, deterioration, and preservation« read at the annual meeting of the International Institute for Conservation of Historic and Artistic Works – American Group, held in Chicago, June 6–8, 1966. It was first printed in the *Guild of Book Workers Journal*, vol. 5, no. 1, Fall, 1966. It has been revised and brought up to date for publication in *Restaurator*.

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