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Conservation of Library and Archive Materials and the Graphic Arts

Edited by

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Society of Archivists
Institute of Paper Conservation

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Series Editors' Preface

The conservation of artefacts and buildings has a long history, but the positive emergence of conservation as a profession can be said to date from the foundation of the International Institute for the Conservation of Museum Objects (IIC) in 1950 (the last two words of the title being later changed to Historic and Artistic Works) and the appearance soon after in 1952 of its journal *Studies in Conservation.* The role of the conservator as distinct from those of the restorer and the scientist had been emerging during the 1930s with a focal point in the Fogg Art Museum, Harvard University, which published the precursor to *Studies in Conservation, Technical Studies in the Field of the Fine Arts* (1932—42).

UNESCO, through its Cultural Heritage Division and its publications, and always taken a positive role in conservation and the foundation, under its auspices, of the International Centre for the Study of the Preservation and the Restoration of Cultural Property (ICCROM), in Rome, was a further advance. The Centre was established in 1959 with the aims of advising internationally on conservation problems, co-ordinating conservation activities and establishing standards and training courses.

A significant confirmation of professional progress was the transformation at New York in 1966 of the two committees of the International Council of Museums (ICOM), one curatorial on the Care of Paintings (founded in 1949) and the other mainly scientific, (founded in the mid-1950s) into the ICOM Committee for Conservation.

Following the Second International Congress of Architects in Venice in 1964 when the Venice Charter was promulgated, the International Council of Monuments and Sites (ICOMOS) was set up in 1965 to deal with archeological, architectural and town planning questions, to schedule monuments and sites and to monitor relevant legislation.

From the early 1960s onwards, international congresses (and the literature emerging from them) held by IIC, ICOM, ICOMOS and ICCROM not only advanced the subject in its various technical specializations but also emphasized the cohesion of conservators and their subject as an interdisciplinary profession.

The use of the term *Conservation* in the title of this series refers to the whole subject of the care and treatment of valuable artefacts both movable and immovable, but within the discipline conservation has a meaning which is distinct from that of restoration. *Conservation* used in this specialized sense has two aspects: firstly, the control of the environment to minimize the decay of artefacts and materials; and, secondly, their treatment to arrest decay and to stabilize them where possible against further deterioration. Restoration is the continuation of the latter process, when conservation treatment is thought to be insufficient, to the extent of reinstating an object, without falsification, to a condition in which it can be exhibited.

In the field of conservation conflicts of values on aesthetic, historical or technical grounds are often inevitable. Rival attitudes and methods inevitably arise in a subject which is still developing and at the core of these differences there is often a deficiency of technical knowledge. That is one of the principal *raisons d'être* of this series. In most of these matters

ethical principles are the subject of much discussion, and generalizations cannot easily cover (say) buildings, furniture, easel paintings and waterlogged wooden objects.

A rigid, universally agreed principle is that all treatment should be adequately documented. There is also general agreement that structural and decorative falsification should be avoided. In addition there are three other principles which, unless there are over-riding objections, it is generally agreed should be followed.

The first is the principle of the reversibility of processes, which states that a treatment should normally be such that the artefact can, if desired, be returned to its pre-treatment condition even after a long lapse of time. This principle is impossible to apply in some cases, for example where the survival of an artefact may depend upon an irreversible process. The second, intrinsic to the whole subject, is that as far as possible decayed parts of an artefact should be conserved and not replaced. The third is that the consequences of the ageing of the original materials (for example 'patina') should not normally be disguised or removed. This includes a secondary proviso that later accretions should not be retained under the false guise of natural patina.

The authors of the volumes in this series give their views on these matters, where relevant, with reference to the types of material within their scope. They take into account the differences in approach to artefacts of essentially artistic significance and to those in which the interest is primarily historical or archaeological.

The volumes are unified by a systematic and balanced presentation of theoretical and practical material with, where necessary, an objective comparison of different methods and approaches. A balance has also been maintained between the fine (and decorative) arts, archaeology and architecture in those cases where the respective branches of the subject have common ground, for example in the treatment of stone and glass and in the control of the museum environment. Since the publication of the first volume it has been decided to include within the series related monographs and technical studies. To reflect this enlargement of its scope the series has been renamed the Butterworths Series in Conservation and Museology.

Though necessarily different in details of organisation and treatment (to fit the particular requirements of the subject) each volume has the same general standard which is that of such training courses as those of the University of London Institute of Archaeology, the Victoria and Albert Museum, the Conservation Center, New York University, the Institute of Advanced Architectural Studies, York, and ICCROM.

The authors have been chosen from among the acknowledged experts in each field, but as a result of the wide areas of knowledge and technique covered even by the specialized volumes in this series, in many instances multi-authorship has been necessary.

With the existence of IIC, ICOM, ICOMOS and ICCROM, the principles and practice of conservation have become as internationalized as the problems. The collaboration of two Consultant Editors, W T Chase, Head Conservator, Freer Gallery of Art, Smithsonian Institution, Washington, and Bernard M Feilden, Former Director of ICCROM, will help to ensure that the practices discussed in this series will be applicable throughout the world.

Acknowledgement

The cost of drawing the line diagrams and printing the colour plates in this book was contributed by the International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome (ICCROM).

ICCROM

Part I

Introduction

Guy Petherbridge

This publication constitutes the proceedings of the Cambridge 1980 International Conference on the Conservation of Library and Archive Materials and the Graphic Arts — the first devoted exclusively to this subject. As the impetus leading to this event and determinining its character represents a significant stage in the history of the modern conservation discipline, a selective outline of major contributory factors may be useful as introduction.

The conservation discipline: theoretical and historical background

In the centuries before our own the predecessors of those now working in the field of conservation of historic and artistic works were usually artisans practising restoration as an aspect of various traditional trades — as cabinet makers, musical instrument makers, bookbinders, etc. Many of their traditional skills and attitudes regarding standards of workmanship or the appearance of a restored artifact have persisted as elements of this craft heritage have been assimilated into the conservation discipline of our day — sometimes in conflict with its standards, but often, especially in the case of the manual skills, as the very basis of the conservator's works. The trades and practices of restoration continue, their common primary ideal being to repair an object in such a manner that the viewer or user is unaware of such intervention. This can be accomplished either by skilful facsimilie work or by substantial reconstruction of the original in what patron or client and restorer consider to be the style or effects most desirable in the particular historical or aesthetic genre.

The last fifty years or more, however, have witnessed an increasing divergence from such perceptions and practices amongst many concerned with the study and care of cultural property, manifested in the development of the museological philosophy and occupation termed 'conservation'. Profound concepts and strict working principles have been formulated which stress the preservation of the original *and* acquired characteristics of an artifact which together constitute its individual nature and are a testament of its unique history. Thus it is considered that conservation should be restricted to treatment necessary to ensure the object's existence with the minimal possible deterioration in a protective environment. There should be no destruction of constituent materials and structure just to improve its appearance, and no faking of missing elements without extensive consideration and investigation of its historical and cultured context.

While the philosophy can be applied in a relatively straightforward manner when dealing with much material of primarily historical and intellectual significance (such as archival documents), its application becomes more complicated in other cases — such as that of musical instruments where substantial material restoration may be necessary for the reproduction of historical sound quality, or that of visual art works where features created to induce an

aesthetic or numinous response may be obscured by later disfigurings which may be erased by conservation treatment even though falling into the category of historical evidence. Also to be taken into consideration are the attitudes of the artists or culture from which a work emanates, there being instances in which the creators or traditional custodians do not sanction an artifact continuing into the future in a static, unageing or 'perfect' state. Although sometimes difficult to resolve, these very questions arise in response to the fundamental bias of modern conservation principles: *an artifact should be preserved rather than restored.* The stance in favour of neutrality or limited intervention has an added legitimacy in that it does not prejudice future generations' chances to impose differing sets of values in the perception and treatment of cultural property.

Parallel with the formulation of these 'ethical' considerations, as they have come to be known, has been considerable development in scientific instrumentation and in techniques for the analysis and documentation of materials and structures, and important advances in the application of chemical and physical knowledge to the safe solution of preservation and conservation problems. The educational basis expected of conservators has undergone a transformation corresponding to these changes in attitudes, working tools and methods. Conservation practitioners have developed an image of themselves as belonging to a unified profession (as distinct from a trade), particularly through the formation a few decades ago of the International Institute for Conservation of Historic and Artistic Works. Although there continue to be circumstances in which conservators are expected to deal with the very wide spectrum of materials and types of artifacts, within the umbrella discipline of conservation there have further developed specialist sub-disciplines named after either a generic context in which artifacts are placed (e.g. archaeological conservation, architectural conservation, ethnographic conservation), a type of artifact or primary constituent material (e.g. paper conservation, painting conservation, textile conservation) or a specialist aspect of general concern to the whole field (e.g. conservation science, environmental engineering).

Until about fifteen years ago the scale of the conservation profession as a whole, its research, advances, discoveries and their dissemination were such that these could, to a satisfactory degree at least, be accommodated under the aegis of broadly-based organizations and publications which encompassed the whole range of conservation activities. These bodies continue to play a most vital role in the unification of an increasingly diversified occupation and in encouraging and facilitating the cross-disciplinary flow and mutual stimulus of ideas and information. They also perform an essential part in the formulation and implementation of common conservation policy objectives.

However, as a natural consequence of the profession's development and growth (connected with the broadening post-World War II and decolonization period museum movement and the increase internationally in the numbers of those involved in art, archaeological and historical research, etc.) certain strong undercurrents of change began to manifest themselves in the late 1960s and 1970s. National and regional groups belonging to international organizations with conservation interests had formed or grown rapidly, and their individual needs were becoming increasingly difficult to satisfy within the format of supra-national parent bodies which they were constitutionally dependent on and ultimately answerable to. These groups tended to become autonomous (examples are the American Institute for Conservation of Historic and Artistic Works and, at a later date, the United Kingdom Institute for Conservation of Historic and Artistic Works), although maintaining similar charters and conceptual and ethical foundations reinforced by close formal links through association and affiliation.

A related phenomenon was the increasing need felt within the conservation sub-disciplines for the organization of independent specialist entities which would better provide a means for them to determine and implement their individual occupational requirements and courses of action. The rapid growth in some of these fields, particularly as a result of the establishment of new training courses graduating new conservators, increasingly articulate concerning the application of their ideas and principles, enhanced this trend. Among the foremost of the pressing problems of which conservators were becoming more and more aware were: the necessity for research and other routes to answers to important questions and issues which could be addressed most satisfactorily within the framework of the subdiscipline itself; more autonomy in policy-making and implementation relating to the needs of the particular sub-discipline than could be accommodated under

the constitutions of existing umbrella organisations; and better means for the exchange and dissemination of occupational-specific information.

Developing activities in paper conservation

Many in paper conservation (paper conservators frequently work with artifacts composed of a much greater variety of materials than just paper — including leather, parchments, photographic media, etc.) were very active participants in these trends.

The profession is a rather diverse one, both as regards the educational and socio-economic background of its members and the principal divisions of material individuals are customarily considered to specialize in: library materials, archive materials, and the graphic arts (the last category is also referred to as prints and drawings, or works of art on paper). In spite of the conceptual developments in basic approaches to conservation in other sectors of the conservation discipline, the majority of conservators of books, documents and art on paper (there have been some notable exceptions) continued to work until relatively recently witrhin the framework of values and techniques rooted in commercial trade practices, particularly those characteristic of the European 19th century.

Within the fields of paper and book production that era saw a number of unprecedented changes in the critera for the selection of materials, the manufacturer's perception of the desired qualities of the finished product and in the production methods themselves. To us, with the critical advantages of a retrospective view of the period, there seems to have been either a lack of emphasis on durability and permanence as a basic feature of quality or at least an awareness of elements in new materials or methods of manufacture which might reduce the length of time a product might last or function as intended. One related factor was the introduction of mass-production systems in trades such as bookbinding (in response to the greatly increased volume of work following mechanization of printing and paper-making and an expanding market) whereby workshop operations (such as the sewing, forwarding and finishing of a book) once carried out in their entirety by a single craftsman were now divided into a number of separated and sometime autonomous procedures each carried out by a different worker. It thus became difficult for the bookbinder at the bench to select, coordinate and integrate all the material and structural elements crucial for a volume's viable functioning. Another tendency was a concern for a pleasingly designed and skilfully executed surface appearance which had priority over the considerations.

Increasingly complex systems were devised to efficiently produce a presentable looking product in large numbers (Victorian case bindings are an example) with little awareness of those matters which often cause present-day conservators of materials from the period so many headaches. In another sphere — that of restoration — the time also saw the introduction of new chemicals into the repertoire of the prints and drawings restorer which produced impressive cosmetic effects but whose properties in affecting works in the long term were little understood or even suspected. These observations are made with no intention of criticising the past — a futile and unrealistic approach. To the Victorians and their contemporaries the very artifacts which have now deteriorated so badly were often productions of the best quality, composed of materials which were economical to produce yet suited secondary industrial processes very well. Coated and ground wood papers of the period, for example, anathema to the modern conservator, were wonderfully innovative uses of raw materials, providing a mass market with a plentiful and cheap commodity which suited machine printing admirably (there were, nevertheless, a few individuals even early in the 19th century, such as John Murray, who foresaw potential problems of permanence).

In occupations such as book restoration, document repair (which was essentially an offshoot of bookbindery practices) and commercial art restoration, in which attitudes and techniques were passed from master to apprentice, it was natural that the values and techniques inherited from this period continued to dominate well into the second half of the 20th century. In spite of developments in other fields such as painting and archaeological conservation, penetration in the present century of the more 'avant garde' conservation concepts and methods was slow (in the case of bookbinding the position was somewhat exacerbated by trade guild standards and training curricula which were not characterized by much innovation except in response to new mass-production systems,

associated machinery and materials). Artisans, particularly the book restorer and archive repairer, were usually from a social milieu which fostered little informed concern for the historical and cultural contexts in which the works they treated had been created or used. Repair and restoration were carried out more often than not without the awareness of such matters but rather in accordance with the values and standards of the artisans' own cultural and craft backgrounds.

However, another current was gaining in strength as the century progressed in tandem with trends in other areas of conservation thought and practice, notably among a small group of book-binder/conservators of whom the names Douglas and Sydney Cockerell and Roger Powell stand out. Evolving further the bookmaking philosophies of the Arts and Crafts Movement in the British Isles, they allowed a more informed perception of the book in all its aspects to be the stimulus for a considered approach to conservation in the modern sense. It is not possible here in the space allotted to name all with major responsibility for the changing stress in approach to the practical care of library and archive materials and art works on paper, but we might cite as other examples those pioneers from various countries involved in the 1898 St Gall conference on manuscript conservation as well as Roger Ellis (the British archive historian whose 1951 exposition on the basic criteria for archive repair helped to change perspectives) as representative of concerned scholars and custodians, and in North America Fletcher Pierre Veitch (who carried out investigations into the care of leather and permanent paper specifications in the first forty years of the century) and William J. Barrow (whose research into the permanence and durability of papers and the protective effects of deacidification and alkaline buffering from the 19650s to the 1970s were foundation contributions to the chemistry of the field) as representatives of pioneering scientists.

Notwithstanding this activity among certain craftsmen, scholars and scientists and the appearance of a number of related publications, an astounding insensitivity to the deterioration and destruction of historical, bibliographical and other significant features continued to be demonstrated by many custodians of libraries and archives. These were (and perhaps one should not restrict oneself to the past tense — the abominable way early and priceless manuscript treasures are displayed in the Library of the Escorial in Spain is an instance) the very people who, by virtue of their professional role in the study and appreciation of such material, beside their responsibility for its care should have behaved with much greater perception and caution. Plain neglect in allowing collections to deteriorate by not comprehending simple patterns of cause and effect in storage, exhibition and use has not been the only destructive factor. In all too many cases the opposite of neglect has had equally lamentable results. Unsuitable binding, rebinding and 'repair' practices with catastrophic consequences for unique historical evidence — often on a massive scale — have been promoted by energetic but unfortunately unthinking curatorial personnel. The situation has not been so severe in the major collections of art on paper, although there long continued a tendency to over-restore and to use cosmetic treatments and display methods whose long-term effects were not adequately known).

An event of major catalytic importance to the field occurred in 1966 — the Florence flood. This disaster, so unfortunate for the many books, documents and works of art destroyed or damaged, had, however, certain fortunate consequences for the future conservation of such material. While, as observed above, a number of individuals and laboratories engaged in paper and book conservation had already evolved a conservation philosophy in line with the mainstream of the other conservation disciplines, the flood rescue effort must be seen as a milestone in the history of the subject (in particular the conservation of library materials) as it enabled a consolidation of basic attitudes as well as the opportunity for further development of materials and techniques, through the meeting and collaboration of conservators from many countries. Amongst these were most leaders of modern book and paper conservation thought and practice. The interchange of ideas and the occasion to compare and evaluate the whole range of current conservation procedures and materials encouraged the formation of an international consensus as to which were the most appropriate, as well as the crystallization of shared conservation concepts (without eliminating divergent approaches, of course).

Because of the wide recognition of the unique cultural and historical importance of the damaged Florentine collections, particularly as witnesses of the Humanists, the Renaissance and early printed book production, the flood rescue and salvage programmes were very much in the public eye and provided an opportunity for the broadening of the influence of those conservators most committed to

the preservation of historical evidence. The international reporting of the rescue work also provided dramatic public exposure of the effective role that conservators play in the preservation of mankind's cultural patrimony in all its forms. This coverage had no little effect in promoting increased post-deluge funding and sympathy for conservation activities. As the participants in the joint effort went on to other responsibilities the network of professional contact in the field ramified, and ideas and techniques continued to develop out of its stimulus.

Many involved, conservators (including a distinguished group of British book conservators amongst whom were Roger Powell and the younger conservation craftsmen Anthony Cains, Christopher Clarkson and Peter Waters, who have perpetuated what has been termed the Powell-Cockerell school), conservation scientists and conservation administrators, subsequently have had a major influence in the formulation of standards in book and paper conservation practice through the example of their work and teaching and their part in the establishment of new conservation facilities (e.g. Trinity College Library Conservation Laboratory, Dublin; Library of Congress Preservation Office, Washington DC; Centro Nacional de Restauración de Libros y Documentos, Madrid; and Centre de Recherches sur la Conservation des Documents Graphiques, Paris).

During these years it became increasingly obvious to many that, in order to advance the occupation's working capabilities and to be more effective in promoting conservation aims, certain major problems had to be addressed with some urgency. Standards (both of ethical approach and workmanship) had to be developed, disseminated, understood and accepted throughout the profession; there had to be a more efficient system for determining research priorities and communication of new research results as well as of new technical developments and historical information; and an organized front was needed in order to press for funding of much-needed conservation programmes and for the implementation of conservation policy.

Among the most effective means to these ends would be a specialist publication programme devoted exclusively to the broadening and multifarious needs of this particular sub-discipline. The current conservation publications (principally periodicals) usually were only concerned with works on paper and related materials as a minor segment of the whole spectrum of conservation interests. No matter how useful such publications have proved, there was just too much happening and too much potential in the sphere of paper conservation for them to adequately cope with. Although from the 19th century a fairly substantial literature had developed relating to the problems and treatment of library and archive materials and the graphic arts (of which a major bibliography was compiled by the Cunhas in the late 1960s and 70s) — documenting a gradual transition from a general orientation favouring restoration to an approach biased towards preservation and conservation — the first major achievement in producing a regular, serious international publication devoted exclusively to paper and related conservation studies was the founding of the Danish journal *Restaurator* in 1969. Other smaller regional specialist publications also began to circulate during this period, such as the IADA German-language bulletin and the Italian bulletin of the Istituto di Patologia del Libro in Rome.

The status of the practising paper conservator, particularly in British archives and libraries, also needed bolstering — both as regards the conservator's self-image as a professional and as traditionally perceived within the hierarchy of cultural institutions. The inability to conceive that the conservator has a truly professional role to perform — in the way society has come to view those occupations termed 'professions'— has often reduced the conservator's ability (both as an individual and as part of a larger occupational group) to realise its full potential in advancing the care of individual collections and cultural property in general.

This situation may be attributed to a number of factors, of which the most important has been the low level of formal educational opportunities and qualifications of many paper conservators. With few exceptions, those coming from a trade or craft background via the apprenticeship system (both in private and institutional workshops), although possessing the manual skills which constitute the very foundation of the conservator's working abilities, customarily perceived themselves and were perceived by others as 'simply' technicians who, because of their traditionally low hierarchial position and lack of formal education on a par with that expected of those occupying curatorial or administrative positions, were not considered capable of influencing or contributing in any executive capacity to the formulation of conser-

vation policy. Worse than that, it was often difficult to convince authorities of the need for even elementary workshop and safety facilities because of the low formal status accorded the occupation. Craftsmen in such straits were additionally hindered because they were often not fully articulate in the concepts and dialectic considered appropriate to those involved in cultural decision-making and management (nor did they participate in their life-style). Pay scales were correspondingly unrealistically low for the level of experience and responsibilities involved. Although there were a small number of extremely distinguished conservators in private practice, even these were often considered by the world of institutional authority as somehow tainted by being 'trade' or 'commercial'.

Such problems were not encountered to any great extent by conservation scientists, who conformed to higher-echelon educational and social ideals. It did, however, give certain of these individuals a somewhat undeserved prominence and degree of influence, both within and outside the ranks of the profession, at the expense of the contribution, actual or potential, of experienced conservation craftsmen. Paper conservation's uneven occupational image was made even more complicated by the entry of increasing numbers of conservators in the 1970s with an advanced formal educational background (having graduated from the recently established conservation training courses at the tertiary level). The majority of these graduates expected to be accorded professional status and remuneration — although emphasis on scientific and cultural/historical studies in their conservation training (admirable and necessary as this is) usually meant a relatively limited time spent on the acquisition of the manual skills and empirical knowledge which were part of the essential stock-in-trade of the traditionally-trained conservation craftsman.

The above were among the principal reasons why the formation of a specialist professional society was thought by many to be necessary in helping the promotion of a better educational balance and the fostering of an awareness of belonging to a unified occupational group with major responsibilities. This enhancement of the conservator's power and ability to function was deemed especially necessary as it was (and still is) painfully apparent that much progress and impetus for progress in the development of conservation facilities and programmes and broader institutional, regional, national and international policy has emanated from within the conservation profession itself rather from the sphere of those traditionally assigned executive responsibility for cultural property — the scholarly, curatorial, administrative and political sectors.

The Institute of Paper Conservation

Until the spring on 1976 no international specialist organisation existed to address the situations outlined above. At that time British paper conservators decided to respond by forming a Paper Group as a section of the United Kingdom Group of the International Institute for Conservation of Historic and Artistic Works. In December 1977 this became the independent Institute of Paper Conservation, functioning as the principal international body representing those concerned with paper and related conservation matters and preserving close links with other conservation organizations. Its intention is to provide a forum for the exchange of information and ideas in the main field of paper conservation (works of art on paper, archive and book conservation) and a focus for professional awareness that will be helpful to conservation craftsmen and scientists as well as to curators of cultural institutions, collectors and commercial entities involved with conservation.

Many aspects of its constitution are similar to those of previously established conservation organizations, but there are some significant differences in emphasis. One of these is the formal acknowledgement of those involved in the manufacture and distribution of conservation materials and in other conservation-related commerce as an integral part of the conservation system as a whole. This was long overdue. Only through full collaboration will the best materials and equipment be produced and made available. Another sector of the merchant world must also be integrated — the art dealers, antiquarian booksellers etc., who as clients of the conservation profession must be encouraged full access to the range of contemporary conservation knowledge and its philosophical trends for the good of the artifacts in their temporary custody.

Other changes of emphasis are demonstrated in the Institute's publication programme. Its annual journal, *The Paper Conservator,* differs somewhat from previous conservation publications by taking a fresh approach in confronting the full scope of

the working realities of the paper conservator, rather than concentrating primarily on new discoveries and advances in scientific research and technical matters. The existing literature had tended to neglect much-needed documentation of established techniques, thus denying the profession knowledge of the full extent of its accumulated resources of manual craft skills and experience. Stress on scientific and related technical achievements had also tended to restrict full recognition of the real contribution and importance of many distinguished conservation workers who were not participants in the more spectacular 'breakthroughs' most frequently accorded the limelight.

The Paper Conservator was designed to redress these omissions and also to provide coverage in other neglected areas, such as the historical and ethnographic documentation of structures and materials, historical and aesthetic awareness and its relationship to the interpretation of evidence, as well as philosophical approaches to conservation. Occupational safety and health was also a prime concern. The publication programme was planned to actively aid and encourage the development of writing and publication skills of potential contributors. In the past those with an academic training or inclination had been advantaged by being already equipped with these abilities, and consequently their prominence in the published literature had tended to give a somewhat lopsided view of the knowledge and accomplishments of the profession as a whole.

The Cambridge 1980 Conference

Preceding the formation of the Institute of Paper Conservation, the Society of Archivists (a British body whose members belonged to the realm of professional archivists) formed a Technical Committee in 1959 which concerned itself with conservation. In 1973 the Society instituted an In-Service Training Scheme for Archive Conservators working within its member institutions. Since 1959 the Society has organized an annual meeting for archive conservators which over the years has become the most important venue of any duration in the British Isles for the exchange of information relating not solely to archives but to a wide range of paper conservation matters. It now draws speakers and participants from all sectors of the profession, with much collaboration with the Institute of Paper Conservation since the latter's foundation.

As the Institute became established as a functioning part of the conservation world, there was an increasing volume of requests that it hold an international conference to consolidate much that was being achieved. Although conservation conferences on a regional, national or international scale had been held on both general and specialist conservation topics, a major international conference specifically devoted to paper conservation had never been organized (although the 1967 Lisbon Conference on the Conservation of Painting and the Graphic Arts held by the International Institute for Conservation of Historic and Artistic Works had covered several aspects). The desires communicated by members of the Institute of Paper Conservation coincided with the Society of Archivists' contemplation of plans for their annual meeting in 1980 and culminated in the joint sponsorship by both bodies of the Cambridge 1980 International Conference on the Conservation of Library and Archive Matrials and the Graphic Arts. This was held from September 22-26 1980 with over 500 participants from 38 countries.

As those who have attended such conferences are aware, the publication of their collected papers does not provide a complete record of the occasion. Much of their essential character is contributed by discussions, formal or informal, through audience participation as well as by the opportunities for personal contact. Little of this activity can be transformed into print successfully. Nevertheless, published conference proceedings do provide permanent documentation of lecture presentations for both delegates and a wider range of readers and indicate the event's calibre and preoccupations.

Although educational by nature, the Cambridge 1980 conference was not planned as a basic orientation course and these selected papers are not presented as a basic primer or to be comprehensive in such a wide-ranging field. The meeting's principal aim was to provide a forum for those professionally occupied with the preservation and conservation of paper and related materials to discuss and assess the most topical present concerns and the current technical and scientific repertoire of the discipline. The hope was that, from this assembly of so many people from so many places, further progress would be made in forming a consensus of opinion as to what the present and immediate future priorities in the conservation of library and graphic materials and the graphic arts should be.

There was to be a dominant theme, but subjects and speakers (each of whom had played a noteworthy role in his or her area of expertise) were selected to present the foremost philosophical, technical, scientific and educational concerns of the profession's principal divisions. It was the intention to underline and focus throughout not just on technical aspects but on fundamental ethical and related broader issues by the degree to which conservation preservations, implicitly or explicitly, took these into account as a premise or consideration. No attempt was made to avoid possible controversy. In fact, only through such opportunities for argument, comment and dialogue (in this case through audience/platform interaction) can the realities of this conservation business be really confronted to an extent which may enable substantial agreement on common approaches and policies.

It was not possible, because of the breadth of the field, to treat each of its sub-divisions in a uniform way, nor is the coverage of any of these comprehensive. The collected papers should, nevertheless, provide a picture or cross-section of the main concerns and achievements in our subject at the start of the 1980s.

The proceedings are divided into four principal groupings, **Paper**, **Vellum and Parchment**, **Books and Bindings** and **Modern Records**, followed by an example of **Conference Discussions**.

The section on *Scientific Developments* in paper conservation presents major recent developments in technical treatment mechanisms: the use of enzymes to release adhesives and innovative uses of liquid ammonia in increasing paper permanence. Much conference discussion was generated by questions relating to the effects, beneficial or adverse, such treatments might have on various features of artifacts so treated.

Contemporary endeavours in the conservation of graphic arts were represented by a number of important contributions. Studies under the heading *Conservation Treatments* comprise four relating to the cleaning of works of art on paper and two giving procedures for the repair of illuminated Indian and Islamic manuscript leaves. Of the former group, two are case reports of actual conservation treatment: one dealing with problems characteristic of many 20th century works — as represented by a Picasso collage — and the other a unique example of the salvation of paper artifacts in what is really an archaeological context — trade prints rescued after being abandoned in the 16th century on the Arctic island of Nova Zembla. Two other papers examine a further subject of much concern to art-on-paper conservators — the bleaching of paper — one on colour reversion of paper following chemical bleaching treatments and the other on alternative solutions to conventional bleaching techniques using sunlight.

In some cases, conference contributors were invited to give a general overview of the subject of special current relevance, such as the section devoted to the *Alkaline Buffering* of paper, which includes synopses of the state of knowledge concerning aqueous and non-aqueous deacidification as well as a paper on a major development in mass deacidification at the Public Archives of Canada.

The section entitled *Mounting and Storage of Art on Paper* outlines the range of attitudes, techniques and materials utilized in the display and storage systems of two major collections of art-on-paper. A third contribution, by Carlo James, regarding the mounting and storage at the Fondation Custodia, Institut Nèerlandais in Paris, is not included but was published in the Cambridge 1980 conference preprints.

A section on *Leaf-casting* gave the opportunity for a brief account of the early history of this process by one of its principal pioneers, a description of one of the main developments in leaf-casting apparatus (the Vinjector system of the Centro Nacional de Restauración de Libros y Documentos, Madrid) and a detailed presentation of the methodological consideration in analysis, specification and calculation in the preparation of leaf-casting pulp. The Spanish paper, unfortunately, is not included here because of its brevity.

One area which up till now has been notably deficient in didactic information is that of the preservation and conservation of skin materials used in documents, books and works of art — leather, vellum and parchment. The conference tried to address this situation to some degree by including contributions on the *Repair* of vellum and parchment, dealing with the repair of vellum manuscript leaves, the controversial use of polyethylene glycol in the restoration of the manipulative characteristics of parchment and preliminary notes on the structure of vellum and the effects of various solvents. A related section approaches the topic of the *Binding, Handling and Display* of vellum and parchment with a paper

on the preservation and display of single leaves and fragments and another on considerations in the binding and storage of vellum-leaved books.

Although many of the meeting's sessions and individual presentations considered — to a greater or lesser extent — basic philosophical and ethical issues, two parts of the conference were dedicated specifically to this theme: priorities in *Book Conservation,* and a panel discussion on ethics in art conservation. Both allowed persons with potentially differing occupational viewpoints to express their opinions and experience. Unfortunately, the proceedings of the latter gathering, although containing many very pertinent and revealing ideas, cannot be included here because of the difficulty of successfully producing a printed version.

The subject of *Books and Bindings,* besides the papers on priorities, includes a section on *Bookbinding Leathers;* as part of the attempt to help fill the gap in the knowledge of factors affecting the conservation of leather-bound books, this represents significant instructional material describing leather structured, manufacture and mechanisms of deterioration.

The vast subject of the treatment of *Modern Records* imposed the selection of a limited but representative group of presentations. These include papers concerning two very diverse aspects of the consideration of *Photographic* processes in the realm of conservation and preservation, one on the role of micrographic records and the other on the conservation of silver gelatine prints. Three papers constitute the section relating to modern *Library and Archival* conservation: an essay recording the development of conservation policy in an American university library, an account of the treatment of modern records in India, and considerations in designing and selecting environmental control systems. Peter Waters' paper assessing archival methods of treatment could not be included but his related publication should be consulted: 'Archival methods of treatment for library documents', in *Preservation of Paper and Textiles of Historic and Artistic Value II,* J. C. Williams (Ed.), American Chemical Society, Advances in Chemistry Series No. 193, Washington DC, 1981, pp. 13-23; and *Past and Present Support Methods for Archival Documents: A Review,* Library of Congress Publications on Conservation of Library Materials, Conservation Workshop Notes on Evolving Procedures, Series 700, No. 1.

Of vital concern to the paper conservation profession is the training of conservators. A conference session on education enabled the presentation for the first time in one venue of the approaches, curricula and training activities of six major teaching institutions or programmes: the Society of Archivists' In-Service Training Scheme for Archive Conservators; the Centro Nacional de Restauración de Libros y Documentos, Madrid; the Winterthur/University of Delaware Art Conservator Training Program; Camberwell School of Art and Crafts, London; the Archival Institute of Training of the National Archives of India; and the Department of Graphic Restoration of the School of Conservation, the Royal Danish Academy of Fine Arts, Copenhagen.

Space restraints preclude this section appearing in this volume, but the papers were published at length in the Cambridge 1980 preprints. The conference format permitted constructive platform/audience discussion regarding such questions as the merits of the more traditional 'on the bench' training procedures, and ways in which these might be incorporated into more formal academic systems which provide the very crucial scientific and historical training now required of a fully qualified conservator. The problem of relating the supply of newly-trained personnel to the actual demand or present capabilities of institutions or other employment opportunities was also stressed. Although the amount of material requiring protection and treatment is overwhelming, there needs to be better coordination between all responsible to match the number of trainees to the work in an all-embracing conservation strategy at both regional and national levels, coupled with a stringent effort to maintain standards achieved at so much trouble over the years.

To give non-participants in the Cambridge 1980 conference as least some idea of the character of the informal discussion sessions which coincided with and supported the lecture programme, an account of discussions and presentations relating to the deacidification of paper artifacts is appended.

Future perspectives and priorities

As noted above, the assembly of so many concerned with the conservation of library and archival materials and the graphic arts from a wide international and professional spectrum provided a chance to observe the present state of the field and

to highlight both its achievements and major persisting problems. In recent years since the founding of the Institute of Paper Conservation and other related phenomena significant advances have been made and certain goals have become within reach.

The proliferation of publications has been most noteworthy. From a situation a relatively short while ago where the available current literature was sparse or uneven in its coverage because of its preoccupations with the newest scientific/ technological achievements, we now already have a range of well-presented resource information essential for the paper conservator's full awareness of the tools, techniques and fundamental concepts of his profession. Many have participated in this publishing endeavour — individual conservators and scientists, professional societies, publishing houses and institutions. Playing a particularly prominent role has been the Library of Congress Preservation Office, the Smithsonian Institution's Conservation Analytical Laboratory, the Canadian Conservation Institute, the Institute of Paper Conservation and the American Chemical Society. One of the more recent developments characteristic of this publishing boom is the praiseworthy preparation by the United Kingdom's Crafts Council of a series of books designed to teach conservators (in all fields) the basic science their occupation now requires.

Scientific and historical research continues with increasing response to demands that the actual working realities of the conservator be emphasized and confronted. Contacts, through the media of conferences, workshops, lectures etc., have also grown tremendously. A recent vigorous development, following the earlier founding of such bodies as the Internationale Arbeitgemeinschaft der Archiv-, Bibliotheks- und Graphikrestauratoren (IADA) and the Institute of Paper Conservation, is the formation of the Paper and Book Specialty Group within the American Institute for Conservation of Historic and Artistic Works.

While there is an ever-continuing need for further progress in all these respects, and although paper conservators will have to be *extremely vigilant* in the maintenance of working and training standards, at last we have reached a position where, if a conservator does not operate from a knowledge of the full basic range of tools, techniques and accepted professional principles, this is no longer because the information is not accessible but because he or she has not exploited existing sources of information and avenues of communication.

The body of qualified, articulate, experienced conservators, equipped to deal with and advise on most aspects of paper preservation and conservation matters, continues to grow (although some so-called conservation courses irresponsibly churn out badly-trained students). Although we have undoubtedly reached a high plateau of accomplishment, we must consider the ultimate and real purpose of the conservation discipline. There are certain fundamental concepts and aims which we risk losing sight of.

It is not enough for those involved in paper conservation (in whatever capacity) to be well-trained, capable, dextrous, versatile, historically and aesthetically aware; *their full potential must be activated so that they are effective* in terms of the overall needs and the enormous scale of the problems inherent in the conservation of our written and printed heritage in its global totality.

It is not just a question of being able to preserve items on an individual or relatively small-scale basis. The perpetuation of society as we are accustomed to conceive or idealize it is dependent to a very large extent on the preservation *en masse* of our accumulated group memories and consciousness stored in the form of the written, printed and otherwise recorded word or symbol. This is the ultimate and enormous task of the paper conservation profession, and will remain so long as this cultural and economic database remains in the materials and formats we know to this date. Of all inherited and contemporary property of artistic, historic and informational significance, by far the greatest number of artifacts are executed in materials which presently fall within the province of the paper conservator. Even modern forms of speech, sound and data recording such as microfilms, records, tapes and disks commonly fall within the responsibility of the discipline, so that our preservation and conservation problem expands infinitely into the forseeable future. If effective measures are not taken to cope adequately with the problems of this heritage as a whole, then the occupation of the paper conservator is ultimately a futile one, condemned by its very own ideals.

This appears to the present editor to be the fundamental contemporary dilemma the profession has to face. We have perhaps reached

a new stage in the history of this work with attendant new priorities — or rather a realignment of stress on certain constant basic priorities. Much of the onus remains with those professionally practising paper conservation to influence public and institutional preservation and conservation policy, particularly regarding library and archive material. However, the need for a coordinated and truly cooperative drive to address the conservation dilemma should be acknowledged by *all* with responsibility, interest or stake in the preservation of our common printed and written resources. Of course, any approach to the overall solution of problems of such enormous dimensions has a built-in element of futility and despair. Nonetheless, all with knowledge, skill and commitment should exert a collaborative effort towards assessing the real magnitude of the situation at all levels and towards planning realistic strategies for coping with it.

One institutional argument that is constantly put forward to explain low levels of preservation and conservation activity is that adequate funding is not available for such concerns. While this may be justifiable if emanating from the bureacracy of a privately-funded holding, it is debatable if put forward by major government-supported collections. We are talking here about a principal property and vital resource of humanity in general. If defence of a society's values and possessions rather than blatant belligerence and oligarchical economic gain is really the motivation for the present overwhelming expenditure on armaments, then perhaps we should allot some of those abundant financial resources to alternative and more constructive methods of defence of our patrimony. As conservation of our environment and wildlife has become a subject to be reckoned with by the public and body politic, so should the conservation of our written, printed and recorded heritage. If everyone with an official executive position of responsibility for the custody of our library and archive holdings actually exerted his or her influence to this problem much progress could be made — both by the realignment of internal institutional policies and by informing, persuading and involving the broader community and its political representatives in order to obtain the necessary extensive funding and support. On an international level better and more realistic systems should be implemented so that the expertise and resources available in certain countries can be *effectively* utilized in others less fortunate in these respects.

Although there are institutions and states which have acknowledged the conservation problem and gone some way to organizing approaches to its solution, progress continues to be hindered elsewhere — often by the very stewards themselves. Even in a country so foremost in advances in conservation knowledge as the United Kingdom, it is continually surprising to see major holdings deteriorate because there is little commitment to preservation and conservation policies on the part of their curatorial, administrative and governing officers. The much-needed funding of conservation budgets is often denied at an appropriate level because funds are allocated (limited though they may be *in toto*) in greater relative proportion to other worthy priorities whose superior merit may be debatable.

There are also alarming instances where, as conservation becomes increasingly fashionable a concept both to society as a whole and in the museum, library and archive world in particular, institutions feel they should conform to trends by appointing conservation staff and by establishing departments bestowed with a conservation or preservation title but with little informed awareness (and sometimes, one may suspect, with little conviction or intent) to support these properly. Associated is the practice of appointing individuals from the traditional curatorial, administrative and emerging technocratic strata of libraries and archives (once again the position is worse in the UK, say, than North America) to preservation and conservation administration positions who do not have adequate training or background in this complex discipline. The language of the modern conservation creed may be easy to learn and use convincingly, but to practise what is preached is a different matter. If an administrator's major interests or involvements are elsewhere or if detailed familiarity with the issues most pertinent to the conservation is lacking then the effectiveness of conservation programmes may be put in jeopardy rather than expedited (even if abundant funding is forthcoming). The situation may be exacerbated when those in authority neglect to involve those most capable of giving professional assistance and instead, by virtue of superior positions within institutional structures and higher-echelon allegiances, monopolize or are over-influential in the formulation and execution of conservation policy.

The recently established graduate programme for preservation administrators in the School of Library Service at Columbia University (in cooperation with the Conservation Center, Institute of Fine Arts, New York University) is the

first to formally and systematically address the need for qualified conservation management. However, as well as librarians, archivists, professional administrators and scholars trained to handle the responsibilities of preservation and conservation organisation, a greater effort should be made to appoint personnel for such roles whose training, experience and main involvements are entirely within the realm of paper conservation. There are a number of conservators and conservation scientists, eminently qualified through their education, working, teaching, consultative and organizational experience who would welcome such an orientation of their skills and potential.

It is no longer realistic to perpetuate outmoded and unmerited hierarchial differences amongst persons of equal degrees of contribution and responsibility in the functioning of a cultural institution. That is not to say that all are capable of operating on the same level nor that a spirit of mutual compromise should not relieve the pressure of pursuing difficult goals, but simply that those with equivalent degrees of knowledge and experience, be these in areas of scholarship, stewardship, administration, conservation etc., should be accorded equal status and equal opportunities to exercize their specialist functions within a framework of mutual recognition, consultation and collaboration. In some areas of the world with developed conservation consciousness and resources, such as the USA, Canada and some countries of continental Europe, there have been significant developments in these respects but in others, particularly the UK, there is room for much improvement.

The seriousness and urgency of the overall preservation and conservation problem as we view it today can only be solved through a fundamental revision and realignment of attitudes — professional, institutional, social and political. There will be no substantial advances in the perpetuation of the written, printed and recorded heritage in its myriad physical manifestations — and surely this is the ultimate purpose of the conservation discipline — without a massive, universal joint effort. The Cambridge 1980 Conference on the Conservation of Library and Archival Materials and the Graphic Arts and this selection of its papers are both products and examples of the movement in this direction.

That the conference could take place was due to the initiative, support and energy of many individuals and organisations. The Society of Archivists and the Institute of Paper Conservation gratefully acknowledge the contribution of the conference speakers, the conference chairmen, Dr Vincent Daniels, Phillip Stevens, Dr R. L. Sykes, Anthony Cains, Anne Harper, Sydney Cockerell, Dr David Cooper, Peter Waters, Eleanor Sayre, Dr Nicholas Pickwoad, Toby Falk, Michael Warnes and Marilyn Kemp Weidner, and the generous financial assistance of the following benefactors, without which the conference would not have gone forward: the Edward Cadbury Charitable Trust, Francis Cator, Conservation Resources International, Inc., the Crafts Council, Professor E. T. Hall's Charitable Trust, Gordon House, Imperial Chemical Industries Ltd, Plastics Division, the Henry Moore Foundation, the Radcliffe Trust, Rank Xerox Ltd, Henry Schroder Wagg and Co. Ltd and Sotheby Parke Bernet and Co.

The editor acknowledges the vigorous and tireless collaboration of his colleagues on the Cambridge 1980 Conference Committee, Lionel Bell (Chairman), Alan Bell (Conference Secretary), Anne Harper (Committee Secretary), Janet Colby, Frederick Marsh, Jane McAusland, Dr Nicholas Pickwoad and Judith Segal, with a particular debt of gratitude to the latter three conservators who, as the Conference Programme Committee, functioned as associate editors in the preparation of both the extensive conference preprints and the papers forming the present volume. Neither the conference nor its publications would have been possible without their commitment and dedication. We all welcome the opportunity the publishers, Butterworths, have given for the conference proceedings to be available to the wider conservation world.

2.1
Scientific Developments

2.1.1 The characterization of enzymes for use in paper conservation

David Grattan, Johanne St. Hilaire, Helen D. Burgess and *J. Clifford McCawley*

Enzymes may become important tools in paper conservation because they act with specificity and rapidity. Proteases act only upon proteins and amylases only on starches. Their use depends on knowledge of the activity of the enzyme and of the composition of the artifact. Performance depends on pH, temperature, the ability to penetrate and the concentration of the enzyme. Commercially available enzymes vary in their composition; they are often mixtures of several enzymes and their activity and specificity may not be precisely known. Small increases in temperature can cause huge increases in activity at the expense of reducing the period during which the enzyme is active; however, if the temperature is high enough, the enzyme denatures and the activity falls to zero. An enzyme for use in conservation ought to be a well characterized reagent, so that treatment conditions can be controlled exactly. In many instances it is important to minimize the soaking period of an object; furthermore, enzymes tend to be expensive; thus it is important to optimize the treatment conditions.

This paper describes the characteristics of some proteases and amylases. The effect of temperature, pH, concentration, the shelf life of enzyme solutions, the effectiveness of enzymes as releasing agents for adhesives and the permeability of enzymes through various kinds of paper were all investigated.

Introduction

Enzymes may well become one of the most powerful tools in paper conservation for adhesive and stain removal, and their use will continue to develop in other areas of conservation. The paper by Segal and Cooper[1] and earlier studies by Wendelbo[2,3] and Sheridan[4] stimulated our interest in developing enzymes for conservation. The initial concern has been to determine whether enzymes are indeed suitable as conservation reagents and to investigate the optimum working conditions. Of major concern is their high potential for causing serious damage to artifacts if improperly handled and, by careful characterization, it is hoped to obviate this danger.

The principal advantages of enzymes are specificity, which enables only one kind of material, such as starch or protein, to be acted on and rapidity of action, meaning that only short immersion periods are necessary.

Enzymes can be reaction-specific and catalyse only one specific type of reaction, such as the breaking of a particular bond in a molecule; they can be substrate-specific and catalyse the reaction of only one compound or class of compounds; or they can be stereo-specific and react with only one stereo-isomer of the substrate.

Their speed of action and their potential for use depend, however, on two factors which may not be well defined. These are the activity of the enzyme and the precise composition of the substrate-containing artifact. Performance is highly dependent on pH and temperature, and is different for each enzyme. Rates of reaction may increase more than fourfold with each 10 °C rise in temperature and can sometimes fall to zero if the pH changes by as little as half a unit. Commercially available enzymes are often found to vary in composition and activity, and

they are often mixtures of several enzymes. Their activity and specificity may not be precisely known. An enzyme for use in conservation ought to be a well characterized reagent. If at all possible, the correct enzyme and conditions for a particular function should be decided before treatment and, if possible, by experiment. Much work is needed to find the optimum conditions and procedures for individual problems. It must be determined if the enzyme has a damaging effect on other substrate materials found in works of art on paper, such as cellulose, water-soluble gums, inks, proteinaceous materials, sizes, adhesives, etc.

The conservator, to date, has found only limited use for enzymes. Other than occasional application of proteases and lipases for the removal of stains, the principal use has been for the release or removal of starch- and protein-based adhesives and sizes. Amylases are used for starch adhesives and proteases for protein-based adhesives. Animal glues, fish glues, bone glues and casein glues are all protein-based adhesives which can be broken down by the use of enzymes.

Protein macromolecules are composed of about 20 different amino acid units which are linked together by the 'peptide bond' to form amino acid sequences characteristic of a particular protein. A protease will cause the hydrolysis of specific peptide links which leads to a decrease in the length of the chain and release of the amino acid residues. The solubility of the protein is enhanced. Proteases, or proteolytic enzymes, can be split into two groups: the proteinases and the peptidases. The former act on the interior peptide bonds of proteins or simple peptides — examples are trypsin and pepsin from animals and papain from plants. Peptidases act on the peptide bonds adjacent to a free carboxyl or free amino group. Examples are aminopeptidase and carboxypeptidase (see *Figure 2.1).*

Starches from most plants are a mixture of two structurally different polymers or polysaccharides: amylose and amylopectin. Both are built up of D-glucose units; however, whereas amylose is a linear polymer, amylopectin is branched with chains occurring at the 1,6-α-linkages. In starches sometimes amylopectin predominates by about 3 to 1. Amylases which appear in α and β forms are enzymes which hydrolyse starches into smaller (lower molecular weight) structural units and, in doing so, destroy the adhesive action. The soluble starches used in conservation are, however, mainly amylose:

$$\text{Amylose} \xrightarrow{\text{amylase}} \underset{\text{polysaccharides}}{\text{dextrin} \rightarrow \text{small straight chain} \rightarrow \text{maltose} \rightarrow \text{glucose}}$$

$$\text{Amylopectin} \xrightarrow{\text{amylase}} \underset{\text{simple fragments}}{\text{straight chain fragments, branched chain fragments}}$$

Figure 2.2 illustrates the action of α-amylase which attacks randomly to give short-chain polysaccharides or dextrins and β-amylase which attacks the non-reducing end of the chain to split off the disaccharide maltose units.

Amylase hydrolyses the α-1, 4-glycosidic linkages in polysaccharides; therefore, amylose, which is a straight-chain polymer of α-1,4-linked glucose units, is completely degraded. Amylopectin, however, which is a branched polymer consisting of short chains of 1,4-linked glucose units joined through the 1 and 6 positions to form a large molecule, is only hydrolysed up to a branch point. This results in branched chain fragments. However, the degree of hydrolysis is sufficient to allow the conservator to remove the starch adhesive.

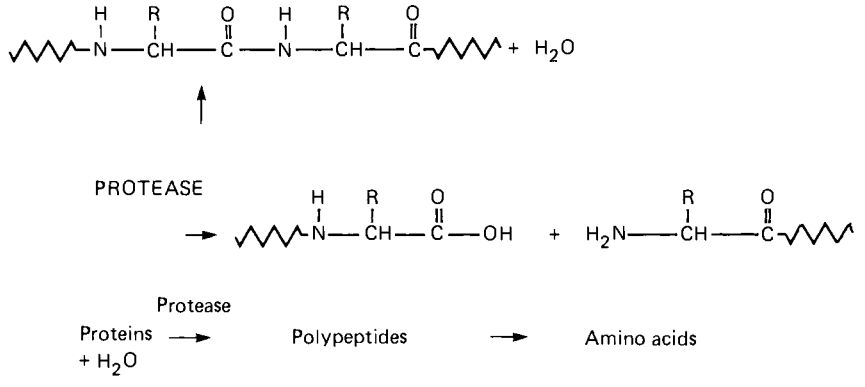

Figure 2.1

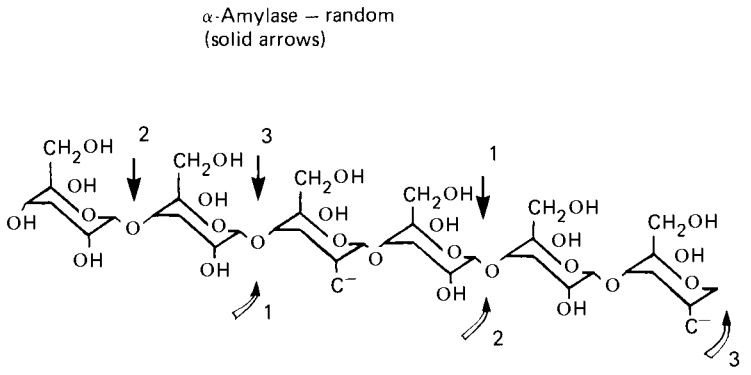

Figure 2.2. Point of attack

These examples illustrate the great specificity of enzymes; they attack *specific* bonds, in *specific* locations and in *specific* ways. Hence their great potential usefulness as precise tools.

For conservation work, it is desirable to use enzymes which attack the molecular chains of adhesives as randomly as possible. From this standpoint, we would suggest the use of α- rather than β-amylase and a protease, such as *Streptomyces griseus* (as used by Segal and Cooper[1]) since it catalyses the hydrolysis of about half the peptide links in the protein chain compared with trypsin (used by Wendelbo[2,3]), which preferentially cleaves at arginine and lysine residues only.

This variation in behaviour makes monitoring of activity problematic. An enzyme with a high activity value may not be as effective as with a lower value if the assay used is not appropriate.

The initial aim has been to carry out classical enzyme characterization studies on the enzymes which have found the most use in conservation; four have been so studied at present — protease pancreatic crude, protease bovine and two proteases *Streptomyces griseus*. All are mixtures of protein hydrolysing or proteolytic enzymes which attack specific peptide linkages adjacent to certain amino acid-derived components of the macromolecule. Protease bovine was studied because it is relatively cheap in terms of activity units per dollar and is available in quite a pure form as a white crystalline solid which yields a clear solution. Protease *Streptomyces griseus* had been previously used by Segal and Cooper[1] and therefore was of primary interest for comparative purposes. This is apparently less pure than protease bovine and furthermore gives a beige-coloured, rather cloudy solution with much less activity per gram. Pancreatic crude was adopted as a replacement for protease bovine. Characterization was carried out by a study of the action of the proteases on the protein casein as substrate. Tyrosine is one of the products of the breakdown of casein and this was quantitatively determined by fluorescence spectrophotometry. (Tyrosine is an amino acid which occurs in most proteins).

This study is being complemented by other investigations of a more practical nature. The first is to measure the release time for paper adhered with various aged and non-aged proteinaceous adhesives to matt-board in enzyme-containing and other solutions. The intention is to show how characterization of an enzyme relates to practical use.

Another important question under study is the part played by permeation of the release-solution through paper. It is important to investigate whether enzymes themselves alter the rate of permeation through paper, what effect sizing has and whether wetting agents are beneficial.

Experimental enzymes used

(1) Protease Bovine (20800) available from the United States Bio-chemical Company, Cleveland, Ohio 44128. Activity 13.8 units/mg.

(2) Protease *Streptomyces griseus* (p-5005), available from the Sigma Chemical Company, Box 14508, St Louis, Missouri 63178. Activity 1.1 units/mg.

(3) Protease — pancreatic crude (p-4630), available from Sigma, as (2), Activity 10 units/mg.

(4) Protease *Streptomyces griseus*, bacterial purified (p-5130) available from Sigma, as (2), Activity 4.4 units/mg.

(5) Gelatinase 16050 fungal origin, United States Biochemical Co., Cleveland, Ohio 44128.

(6) Diastase B39013-32 BDH Bio-Chemicals, 350 Evans Avenue, Toronto, Ontario, Canada M8Z

1K5, diastase from malt (mixed and amylose). Activity 4 units/mg.

(7) α-Amylase Type X-A Fungal crude (*Aspergillus oryzae*) from Sigma, as (2). Activity 36 units/mg.

Protease bovine gave a clear white solution, *Streptomyces griseus* 5005 a brown and cloudy solution and *Streptomyces griseus* 5130 a white and cloudy solution. Unfortunately, protease bovine (no. 20800) is no longer available and the Sigma pancreatic crude was adopted as a replacement. *Table 2.1* shows the cost of one litre of enzyme solution at an activity of 10 units/ml. (Segal and Cooper[1] used an activity of 0.11 unit/ml, one litre of which would cost $0.50 in mid 1980).

Table 2.1. Cost of one litre of enzyme solution of activity 10 units per ml (mid 1980)

		Relative cost (PC 4630 = 1)
S.G. 5130	$24	2.4
S.G. 5005	$50	5
Pancreatic crude 4630	$10	1
P.B. 20800	$0.80	0.8

Characterization of the proteases

In a well-established procedure for the assay of proteases, a known concentration of enzyme was allowed to act on a fixed concentration of casein for a specified time and at a particular pH and temperature. Amongst other amino acids liberated by hydrolysis is tyrosine, present as a residue in ten times the concentration in casein as compared with collagen. Tyrosine can be readily monitored by fluorescence spectrophotometry after an extraction procedure.

A typical characterization experiment was carried out as follows. Stock solutions of enzyme and 1% w/v casein were made up in buffer[5] solutions of the desired pH. For each determination, the enzyme solution was pipetted into a measured amount of casein solution by micropipette. Temperature was maintained constant by keeping the solutions in a water bath at the selected temperature to within one tenth of a degree Celsius. On mixing, a stopwatch was started and termination of the reaction was achieved by adding an equal volume of 6M trichloroacetic acid. After 10 minutes, the solution was centrifuged at approximately 33 000 rpm for 10 minutes. To 0.5 ml of working reagent[6] in a screw-capped tube, 20 microlitres of the supernatent liquid was added. This was incubated at 60°C for 20 minutes in a water bath.

On removal, 2.5 ml of distilled water and 4 ml of 1,2-dichloroethane were added, the tubes were re-capped and vigorously shaken for 10 — 15 seconds, centrifuged for 5 minutes at 3300 rpm and then the clear aqueous layer transferred to a cuvette for the determination of the fluorescence. This was carried out in a Turner Model 111 Fluorometer with a No.7-60 primary filter and a No.58 secondary filter[7]. Each determination was repeated at least three and sometimes up to twelve times until consistency was achieved. The results were corrected for volume by adjusting them to 1 ml, averaged and plotted. This method is a modification of that described by Phillips[6]. The results are plotted as relative fluorescence and this is directly related to the tyrosine concentration: calibration gave 1.04×10^3 relative fluorescence units to 1% w/v tyrosine (assay conditions are summarized in *Table 2.2).*

Table 2.2. Assay conditions for proteases

Temperature: 37°C
pH 7.5 (phosphate buffer)
Time: 1 minute
Casein: 1 mg (1% w/v)
Volume: 1 ml
Enzyme: 1 unit (1000 units/litre)

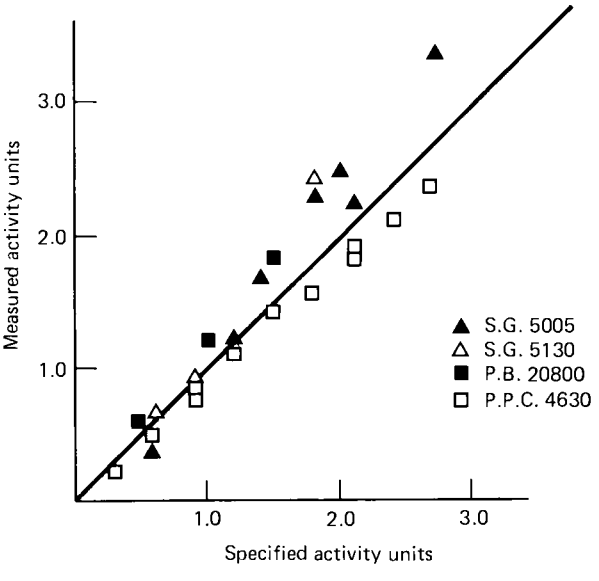

Figure 2.3

In *Figure 2.3* is shown a plot of measured versus manufacturers' specified activity. The solid line is the theoretical 1:1 relationship and it can be seen that agreement is good. Each set of points forms a straight line, each of these lines is very near the theoretical 1:1 line. This validates the assay and calibrates the enzyme at the same time.

At higher concentration of enzyme the measured activity falls below that predicted theoretically. The critical concentration is about 5 units/ml for both proteases studied, a concentration fifty times greater than that used by Segal and Cooper (*Figure 2.4*).

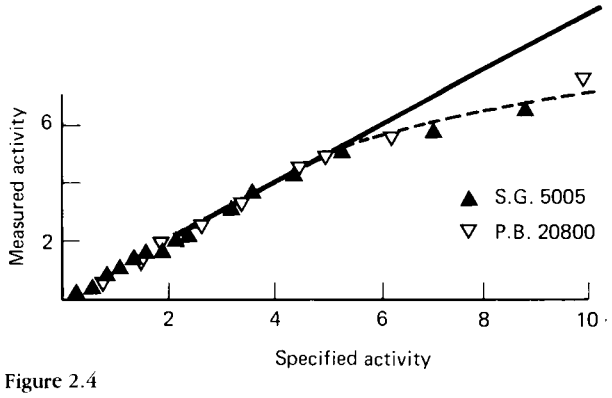

Figure 2.4

This is not a problem for an enzyme intended for conservation use because enzymes are useful at concentrations much lower than 5 units/ml. On a more practical note, solutions of this high strength are prohibitively expensive for conservation work. One litre of such a solution of protease *Streptomyces griseus* costs around $50 (1980) Canadian.

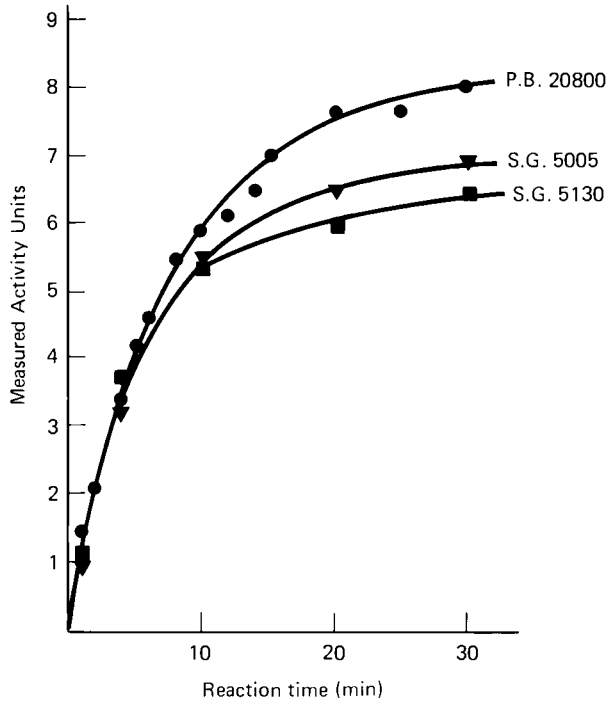

Figure 2.5. The rate of tyrosine production with time.

In *Figure 2.5* the rate of tyrosine liberation (i.e. measured activity) versus time is shown for three enzymes. Reaction proceeded very rapidly at first, but after 7 minutes began to slow down. This decrease in reaction rate occurs for a number of reasons, the chief of which is that the products of the reaction themselves interfere with the enzyme and essentially poison the reaction. Practical consequences are that there is little point in continuing to submerge artifacts in enzyme baths for extended periods. The solutions must be replaced at appropriate intervals.

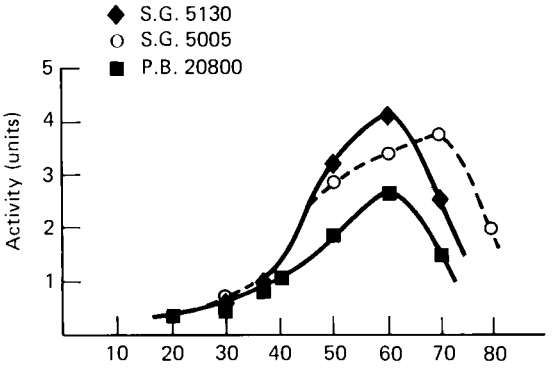

Figure 2.6

In *Figure 2.6* the effect of temperature on tyrosine liberation or enzyme activity is shown. Activity increases steadily with temperature up to 60°C, where enzyme denaturation takes place and, thereafter, the activity decreases rapidly. Perhaps the most important consequence for the conservator is that both enzymes show significant activity at 20°C and can perhaps be effectively used at temperatures as low as this. Little benefit in terms of increased activity is achieved by increasing the temperature to 30°, but at 40°C there is a substantial acceleration. A useful general rule is that enzyme-catalysed hydrolysis (or activity) doubles in rate for each 10° increase in temperature from 20°C to 60°C.

From consideration of the data in *Figures 2.5* and *2.6* it can be deduced that by raising the temperature of the bath at 37° by 10° the effective working time of the solution is halved and, by reducing the temperature to 27°C, the effective working time is lengthened by a factor of two. Where permeation is a problem, these considerations may be of crucial importance.

Figure 2.7 illustrates the dependence of activity on pH. The optimum for *Streptomyces griseus* proteases was found to be around 9.0, but for protease bovine to be 7.5. However, most important is that the enzymatic catalysis takes place over the pH range 5.5 to 11 and that it is very active the range pH 7 to 10.

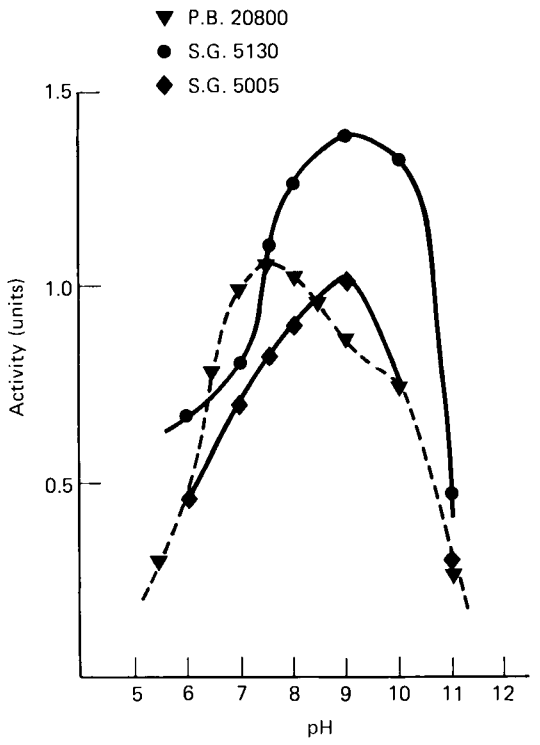

Figure 2.7

In *Figure 2.8* the effect of changing the casein concentration is examined. Conditions were: temperature 37°C, pH 7.5, reaction time 1 minute, and the concentration of protease bovine was 1.5 units/ml. The amount of tyrosine liberated (given by the value of the relative fluorescence) seems to go through a broad maximum at a casein concentration of 1% w/v, which is why this value was chosen for the characterizaton work. However, there is little change in tyrosine liberation with casein concentration. This suggests that variations in the amount of protein substrate will not greatly affect the reaction rate.

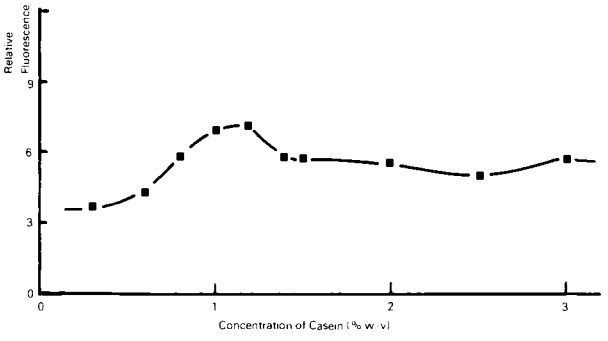

Figure 2.8. Effect of casein concentration on the yield of tyrosine

In *Figure 2.9* the results of a study of the shelf-life of proteases are shown. Two pieces of information can thus be obtained: (1) how long working solutions may be held for and (2) how long enzyme activity will endure in a solution where penetration is poor and the enzyme is delayed in its contact with the protein. The activity was determined with enzyme solutions which were allowed to remain on the bench at 22° or at 0°C over the course of about one month.

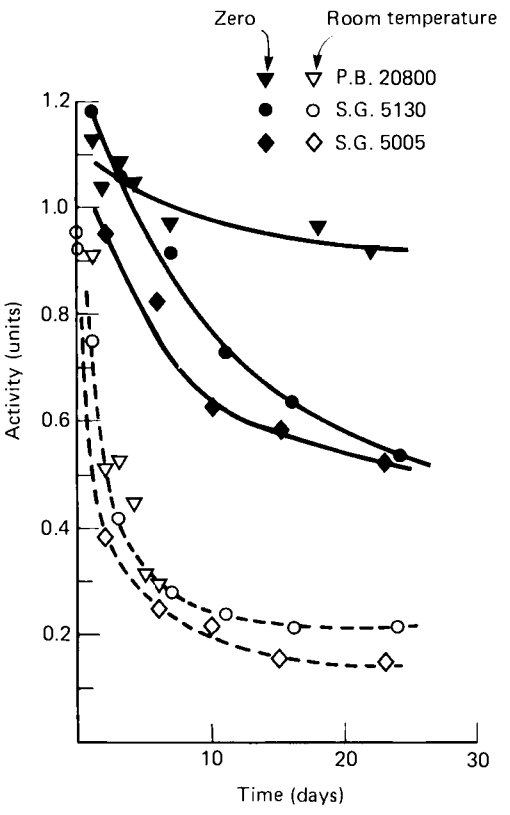

Figure 2.9

At 0°C protease bovine is quite stable, but *Streptomyces griseus* enzyme solutions lose half their activity in one month. At 23°C the solutions lose half their activity in 2 days and it may be predicted that at 30°C they will lose half their activity in 1 day and at 40°C perhaps within half a day. Where penetration is a problem, enzyme solutions may be more effectively used at lower temperatures where the working life is longer.

This means that if enzyme solutions are to be stored, they should always be kept refrigerated and never longer than one or two months. (Enzymes in the solid state are perfectly stable if maintained in dry conditions in a freezer.)

Characterization of the amylases

A procedure similar in character to that used for the proteases was employed for amylases [10], and, likewise, the effects of concentration, time and pH were studied.

Only one enzyme has been characterized: α-Amylase No. A0273 Fungal Crude Type X-A, from *Aspergillus oryzae*. The assay method monitors the quantity of reducing sugars produced by the action of the amylase upon starch under a set of fixed conditions. (Each reducing end reacts with dinitro salicylic acid. This results in a yellow solution.) In *Table 2.3* the assay conditions are summarized.

Table 2.3. Assay conditions for amylases

Temperature: 20°C
pH 6.9 (phosphate buffer)
Time: 3 minutes
Starch: 10 mg (0.5% w/v)
Volume: 2ml
Enzyme: 1 unit (500 units/litre)
α-Amylase Type X-A Fungal Crude (*Aspergillus oryzae)* Sigma Chemical Co. A0273

The measured activity is plotted in *Figure 2.10* versus that specified and the theoretical 1:1 relationship shown. The activity found was 46 units /mg. (For *Aspergillus oryzae,* one litre at the concentration adopted by Segal and Cooper [1], would cost $1.35 (mid-1980 cost)).

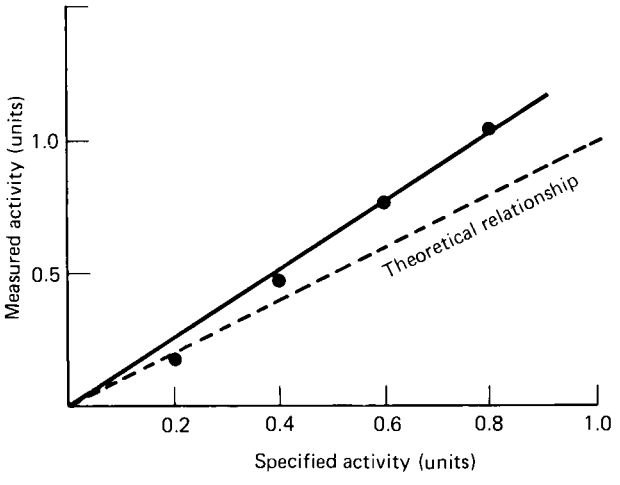

Figure 2.10

Agreement between the specified and experimentally determined activities was not quite as good as for the proteases. However, it was felt that this was in no way caused by inaccuracy of the assay procedure, but rather the variability of the activity of different batches of enzymes. The linearity of the plot gives us confidence in the validity of the method.

Figure 2.11 illustrates the effect of time on activity, that is, the generation of reducing end-groups. At 20°C the activity falls off after about 30 minutes. (The 3 minutes' duration in the standard assay is well within the linear portion of the curve.)

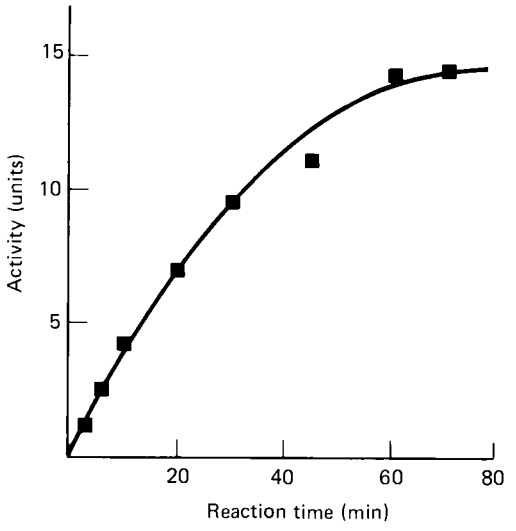

Figure 2.11

Figure 2.12 shows the effect of temperature. As for the proteases, the activity approximately doubles with each increase of temperature at 10°C and at 60°C rapidly falls.

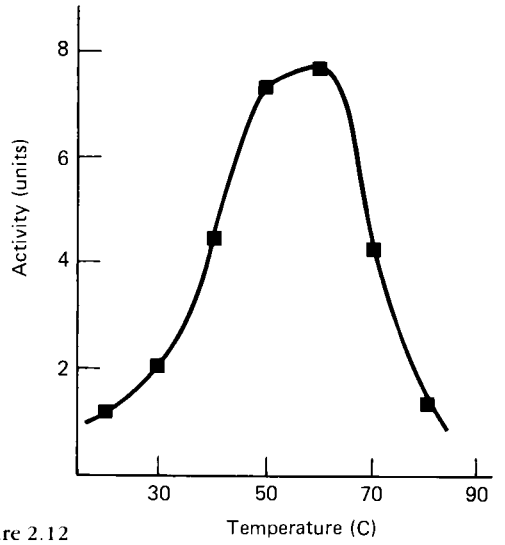

Figure 2.12

Figure 2.13 illustrates the dependence of activity in pH. Again the enzyme is seen to be active over a wide pH range. ALthough more data are needed here, the broad maximum seems to be around pH5.

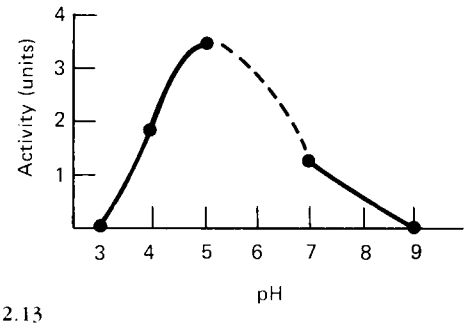

Figure 2.13

Permeation of the solutions through paper

Another important consideration is the ability of the enzyme to permeate through a paper so that it may reach the adhesive upon which it is intended to act. There appeared to be several questions:

(1) Can chromatographic processes occur such that the enzyme proceeds at a slower rate through paper than the solvent?
(2) What is the difference in rate at which liquids pass through various kinds of paper?
(3) Can wetting agents help?

An apparatus was constructed to measure the rate of liquid penetration through layers of paper. This consisted of an arrangement in which several layers of paper were tightly clamped in the horizontal plane between two 4-cm diameter rubber O rings (*Figure 2.14*). The O rings themselves were mounted in two blocks of Plexiglas (2.5 × 18 × 18 cm) with 2.5-cm diameter holes at the centre to allow access of the permeant to the upper and lower surfaces of the paper stack. These blocks were tightly clamped to press the O rings together. The hole in the upper Plexiglas block, above the horizontally mounted paper, provided a reservoir for the permeant and was always filled to the brim to provide a constant head with a hydrostatic pressure of 2 cm of water. An experiment was performed by first mounting the desired amount of paper and then starting a stopwatch as the reservoir was quickly filled. When the bottom surface of the paper stack became damp (or when the second drop of liquid appeared) the stopwatch was stopped.

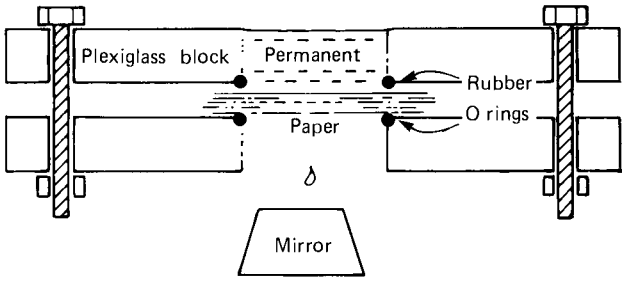

Figure 2.14. Permeation apparatus

In the first experiment, eleven Japanese papers[9] and Whatman No. 1 filter paper were studied with distilled water and then enzyme solutions as permeants. Three or four determinations were made for each paper with different numbers of layers in the stack ranging from 5 to 80 sheets, depending on the flow rate achieved. Permeation was so rapid that it was not seen as a problem in treatment. For the slowest paper, penetration was less than one second per sheet.

In the second part of the study a solution of protease bovine at pH 7.5 was allowed to permeate through a stack of each of the twelve papers studied at room temperature. The presence of enzyme appeared to increase the rate of permeation slightly; this effect was later confirmed and is discussed in the next section. After each experiment, the paper was dried, separated and sprayed with a 0.25% solution of ninhydrin in acetone. This is a simple protein determination test. An intense mauve colour slowly develops over 12 hours at 22°C to indicate the presence of enzyme. No difference was observed between the extent of liquid permeation and the presence of enzyme. The initial evidence is that chromatographic effects are of no importance for enzymes in this application.

Flow through sized paper was found to be much slower and here enzymes and wetting agents play a significant role in determining penetration. Gelatin-sized Takenaga paper was examined and the results are shown in *Table 2.4*.

These results illustrate several points. The effect of the wetting agent, Lissapol NDB, is to reduce the penetration time drastically, but what is also surprising is that gelatinase and protease solutions flow through much more rapidly than distilled water. Thus it would appear that enzymes are acting as wetting agents or perhaps have wetting agents incorporated with them. Since the solution of enzyme with the wetting agent penetrates no faster then the permeant with just wetting agent, it is thought that enzyme action on the size does not have any effect on flow.

The question of whether the wetting agent reduces the activity of the enzyme was investigated by repeating some of the characterization measurements with protease bovine in the presence of 0.1 and 1% v/v Lissapol NDB and Kodak Photo-Flo 200 at 0.5% v/v. No effect was observed.

A starch-sized Japanese Kozo paper was similarly examined and the results are shown in *Table 2.5*. In this experiment the enzyme, diastase, which is a starch-consuming enzyme, is almost certainly

Table 2.4. The time taken for a series of permeants to pass through five layers of gelatin-sized Takenaga paper at room temperature (22°C)

Permeant	Enzyme concentration (units/ml)	Permeation time (min)
Distilled water	0	7.43
As above with 0.1% v/v Lissapol NDB	0	1.60
Protease *Streptomyces Griseus* in pH 7.45 buffer solution	1.36	2.30
As above with 0.1% v/v Lissapol NDB	1.36	1.68
Protease *Streptomyces Griseus* in pH 7.45 buffer solution	6.8	2.57
Gelatinase in pH 7 buffer solution	0.25% w/v	1.98
As above with 0.1% Lissapol NDB	1.25% w/v	1.63

Table 2.5. The time taken for a series of permeants to pass through five layers of starch-sized Kozo paper at room temperature (22°C)

Permeant	Enzyme concentration (units/ml)	Permeation time (min)
Distilled water	0	more than 240
As above with 0.1% v/v Lissapol NDB	0	155
Diastase in pH 6.95 buffer solution	200	20
As above with 0.1% v/v Lissapol NDB	200	11.5

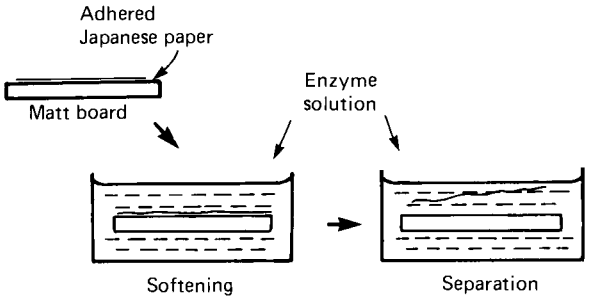

Figure 2.15

affecting the sizing of the paper thereby improving permeability. Again the wetting agent is a considerable aid. By using enzyme solutions with a wetting agent, penetration speed has been increased by more than twenty times.

Releasing action with adhesives

Having completed the detailed characterization of the proteases and amylases, optimum conditions for the use of an enzyme may be selected. To confirm that these are realistic conditions, a more direct series of studies was undertaken. In the first of these experiments, the effect of protease *Streptomyces griseus*, on the bond of the proteinaceous adhesive Nacan 18-8165 (Nacan Products Ltd, 50 Marie Victoria, Boucherville, Québec, Canada J4B 1V5) was studied. This adhesive is used in the paper conservation section of the Canadian Conservation Institute and has working properties typical of an animal glue.

Pieces of paper 5 × 5 cm square with and without size were adhered to pieces of acid-free matt board of similar dimensions. Observations were made at the rate at which the adhesive softened and the length of time which elapsed for separation to occur such that the paper floated to the surface of the bath in the absence of agitation (see *Figure 2.15*). The conditions of the experiment were pH7.5, temperature of 22°, 30° and 40°C, with a protease concentration of 1.1 units ml (0.1% w/v).

Softening took about 3 — 4 minutes for each experiment at 22°C and was independent of the presence of enzyme in the solution. The initial results for release time are shown in *Table 2.5*. For some animal adhesives, such as fish glues, it was noted that release only takes about 10 minutes whatever the composition of the bath. The adhesive softened so quickly that the enzyme reaction hardly speeded it up. With very impermeable paper and adhesives which are hard to remove, release is so slow that the enzyme may lose its activity before complete release is achieved.

The proteases studied functioned most usefully when the release time in water took 1 — 6 hours. The presence of buffer or Lissapol NDB by themselves had little effect (*Table 2.6*). In the third and fourth columns the presence of enzyme is seen to speed up the release dramatically. Lissapol may play a considerable part in this. For the thick Italian Peschia paper it certainly reduced the release time.

The presence of wetting agent was beneficial and this, too, shortened the release time. The most effective procedure would be to use a compatible wetting agent and an enzyme together. The main

Table 2.6. Release time in minutes at 22 °C Nacan hide glue enzyme concentration 0.35 units/ml Lissapol 0.1% v/v.

	Water (+ Lissapol)	Buffer (+ Lissapol)	P.C. 4630 (+ Lissapol)	S.G. 5005 (+ Lissapol)
Kozo non-sized	234 (222)	402 (402)	84 (78)	60 (54)
Kozo Starch-sized	360 (354)	360 (360)	84 (84)	72 (78)
Takenaga gelatin-sized	80 (60)	40 (45)	30 (18)	28 (25)
Peschia non-sized	372 (342)	480 (480)	450 (270)	306 (294)

benefit in increasing the temperature is in the softening of the adhesive. The dramatic shortening of the release times cannot be accounted for by increased enzyme activity only. This investigation is not yet completed and other adhesives, supports and the effect of ageing will be studied.

Conclusions

Using the characterization information shown here the conservator can choose the most favourable conditions for the artifact in question. It is quite clear that enzymes are useful reagents even at room temperatures.

Perhaps the second most useful conclusion is the benefit of using wetting agents to speed the action, particularly with sized papers.

Notes and References

1. Segal, J. and Cooper, D. (1977). The use of enzymes to release adhesives', *The Paper Conservator,* 2, 47-51
2. Wendelbo, O. (1975). 'The freeing of papyri from cartonnage', *Restaurator, 2,* 2, 41-52
3. Wendelbo, O. (1976). The use of proteolytic enzymes in the restoration of paper and papyrus', Doctoral Dissertation, University of Bergen (Norway)
4. Sheridan, J. (1962). *Enzymes as they Relate to the Conservator of paintings,* Exposition of Painting Conservation, Brooklyn Museum
5. Buffer solutions were composed of 12.2 g Na $H_2PO_4(2H_2O)$ and 17.3 g Na_2HPO_4 in 1 litre water. Hydrochloric acid or sodium hydroxide solutions were added to produce the correct pH, as measured by a standard glass electrode with a Fisher Accumet 420 pH meter, calibrated by Fisher Scientific Company Certified Buffer solutions at pH 6, 7, 8, 9, 10 and 11 where appropriate
6. The working reagent consisted of equal volumes of 1.5 M nitric acid, 0.1 M sodium nitrite and a 13% w/v solution of 1-nitroso-2-naphthol in 95% ethanol
7. Excitation of the fluorescence was at 365 nm, with measurement at 525 nm
8. Phillips, R. E. (1977). 'Tyrosine in serum', *Manual of Clinical Procedures,* Turner Associates
9. Japanese paper, Okawara 6006, Hosho 6002, Okawara Student grade 6043, Kitakata 6004, Mulberry 6239, Sekishu White 6058, Chinese Traditional tissue 6048, Kochi 6003, Takenaga (both sized and waterleaf 123 and 1041), Azzo 109, Numbers 6006, 6002, 6043, 6004, 6039, 6058 and 6048 are order numbers of Rembrant Graphic Arts, New Jersey, USA and number 123, 104 and 109 are order numbers of Aiko's Art Materials Import Inc., 714 N Wabash Avenue, Chicago, IL 60611 USA.
10. Bernfield, P. (1955). 'Amylases, α and β, in *Methods in Enzymology,* Chapter 17, Volume 1, Sidney P. Colrick and Nathan O. Kaplan (eds), Academic Press, New York, pp 149-150.

2.1.2 The use of enzymes in partially non-aqueous media

David Cooper, Carolyn King and *Judith Segal*

The technique previously described by Cooper and Segal for the removal of old repairs and adhesive deposits is extended to include cases in which the inks are fugitive in aqueous solutions. The stability of various inks in a number of solvent systems is assessed. The activity of α-amylase and protease in a range of mixtures of water and various organic solvents is investigated, 2-methoxyethanol and propan-2-ol at a concentration of 45% being shown to offer reasonable activity for repair work. Examples of these enzymes in the above solvent mixtures acting on actual library materials, both manuscript and printed, are presented.

Although enzymes were first employed in conservation work only a few years ago, their use is now becoming a routine matter in the authors' unit,[1] and in others throughout the world.[2-4] The ability of enzymes to break down natural substances such as adhesives under very mild conditions is a much-prized one and is being increasingly used in the field of paper conservation.

There are limitations to the present usefulness of this technique, however. One of the most important of these is the necessity to work in aqueous conditions. This may not be of great moment when one is dealing with something as comparatively robust as a printed page, but as soon as one starts to work on manuscripts the constraint becomes very obvious and irksome. A significant proportion of the material a manuscript restorer encounters will be written on in inks which, to a greater or less extent, are not stable under the conditions hitherto found to be optimum for the use of enzymes — essentially soaking in water at 40°C for a matter of some minutes, or maybe several hours.

Many of these inks are, however, perfectly stable in organic solvents such as methanol, acetone, ether, etc. This led us to wonder whether we could adapt our enzyme technique to work in these new, non-aqueous, conditions. This idea did not look, at first sight, at all hopeful. Enzymes are natural catalysts designed to perform certain reactions in natural systems in plants or animals. When using them in conservation, we give them reactions to catalyse as near as we can to those they would perform in their host organism. To make them work we have had to provide them with working conditions as close as possible to their environment *in vivo,* hence the controlled, buffered, pH, the near blood heat temperature and so on. Under these conditions they act reasonably efficiently, but their efficacy drops quite rapidly when even comparatively small departures are made from ideal conditions — say we change the pH by 1 unit, or the temperature by 10°C. It would, therefore, not be surprising if their activity dropped to zero under such a radical change of conditions as that from water to an organic solvent.

Enzymes are proteins, and are virtually insoluble in most organic solvents. Likewise, the adhesives, etc. which are to be broken down are largely insoluble. Since some solution of either the enzyme or the adhesive in the reaction medium must occur before any action can take place, pure organic solvents cannot be used. Fortunately, however, most of the water-sensitive inks, while unstable in completely aqueous media, are acceptably stable in

a mixture of water and a water-miscible organic solvent. The degree of stability varies with the particular solvent chosen and the proportion of solvent to water in the working medium, but typically a mixture of equal parts of water and one of the lower alcohols is satisfactory.

At this point a few trial runs were made using α-amylase in aqueous methanol in an attempt to remove some old repairs attached to a manuscript with starch paste. Greatly to our surprise, some reaction was observed. The repairs were removed, but only by the use of a very large excess (*c.* 80 × normal concentration) of enzyme, applied directly to the reaction site. Enough progress was made, however, to encourage us to carry out a thorough investigation into the potentialities of the technique. This naturally broke down into three stages:

(1) The testing of a representative selection of mansuscripts with a wide variety of solvents, both neat and diluted with water.

(2) The reactivity of various enzymes in the solvent systems shown to be the most suitable.

(3) If the foregoing stages showed sufficient promise, the use of some selected systems on actual manuscript samples.

(1) The stability of manuscript inks in various solvents

Since the conservator may be faced with almost any combination of inks and papers, each of which may be stable to a different solvent or concentration of solvent, a wide range of organic solvents was tested. The results are summarized in *Table 2.7*.

(2) The activity of enzymes in partially non-aqueous media

Initial experiments were conducted with α-amylase, as the majority of cases needing the partially aqueous enzyme treatment were likely, in our experience, to involve the softening of starch adhesives. As preliminary experiments had already

Table 2.7. The stability of various inks in solvent systems
X = fugitive ✓ = not fugitive

	Date	Water	2 methoxyethanol	45% 2 methoxyethanol	45% methanol	45% isopropanol	45% n propanol	1,4 dioxan	45% dioxan	glycerol	50% glycerol	ethyleneglycol	45% ethylene glycol	45% dimethyl formamide	polypropylene glycol 2025	45% polypropylene glycol 2025
Iron gall	1645	X	✓	✓	✓	✓	X	✓	✓	✓	X	X	X	X	X	X
Blue ink	1955	X	✓	X	✓	X	X	✓	X	✓	X	✓	✓	X	✓	X
Blue ink	1960	X	X	X	X	X	X	✓	X	✓	X	X	X	X	✓	X
Blue ink	1922	X	✓	X	X	X	X	✓	X	✓	X	X	X	X	✓	X
Blue/black ink	1938	X	✓	✓	✓	✓	X	✓	✓	✓	✓	✓	✓	X	✓	✓
Blue/black ink	1959	X	✓	✓	X	X	X	✓	✓	✓	X	✓	X	X	✓	X
Blue/black ink	1952	X	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Blue/black ink	1926	X	✓	✓	✓	X	✓	✓	X	✓	✓	✓	X	✓	✓	X
Black ink	1913	X	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Biro blue	1972	✓	X	X	X	X	X	X	X	X	✓	X	X	X	X	X
Biro blue	1952	✓	X	✓	✓	X	X	X	X	✓	✓	✓	✓	✓	✓	✓
Biro green	1966	✓	X	✓	✓	✓	X	✓	X	✓	✓	✓	✓	✓	✓	✓
Biro black	1974	✓	X	X	✓	X	X	X	X	✓	✓	X	✓	X	X	✓
Black typescript	1929	✓	X	✓	✓	✓	✓	X	X	X	✓	✓	✓	✓	X	✓
Black carbon	1929	✓	X	✓	✓	✓	X	X	X	X	X	✓	✓	✓	✓	✓
Purple carbon	1920	✓	X	✓	X	X	X	✓	X	✓	✓	X	✓	✓	✓	X
Black letter heading	1952	✓	X	X	✓	✓	✓	X	✓	✓	✓	✓	✓	✓	✓	✓

shown that the presence of 50% methanol greatly reduced the specific activity of the enzyme, it was important to define more precisely:

(1) The comparative loss of specific activity of the enzyme in other organic solvents which had been found useful in manuscript treatment *(Table 2.7).*

(2) The optimum conditions of pH and temperature which would allow the most effective action of a reasonable concentration of enzyme within a realistic incubation period which was not harmful to the manuscript.

The assay of α-amylase is based on the fact that when the starch is broken down, maltose is produced, which reacts with 3,5-dinitrosalicylic acid to produce a coloured compound, whose concentration can be determined spectrophotometrically.[5]

Aliquots of enzyme solution (at final concentration between 10 and 100 μg/ml depending on organic solvent) were incubated at 37°C with a standard starch solution, final concentration 5 mg/ml, made up to be 50% aqueous buffer (phosphate, pH 7 final concentration .01 Molar) and 50% organic solvent for various lengths of time. The reaction was stopped by the addition of 1 ml of the colour reagent (3,5-dinitrosalicylic acid (1g) in 1N NaOH (40ml) + sodium potassium tartrate (30g) made up to 100 ml with water). The sample was placed in boiling water for 2 minutes, cooled in ice or cold water, diluted 10-fold and the optical density measured at 540 nm. The results were expressed as mg maltose released per mg enzyme, by reference to a standard maltose calibration curve.

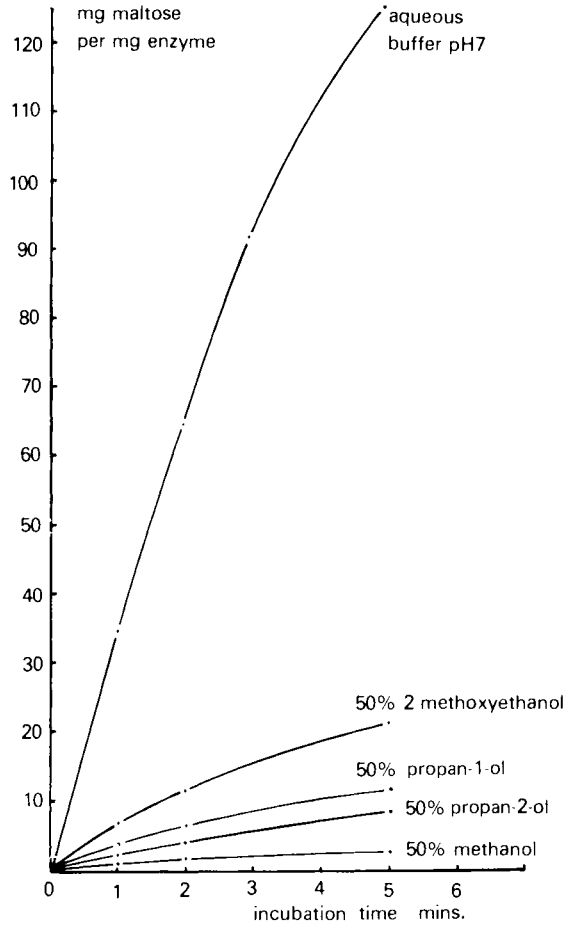

Figure 2.16. The activity of α-amylase in various media at 37°C.

The results for four solvents and aqueous buffer pH 7 are shown in *Figure 2.16.* The initial rate of reaction (the mg of maltose released in the first minute per mg enzyme) was calculated for each solvent, and the results were expressed as a percentage of the initial rate in aqueous buffer at 37°C, as shown below:

2 methoxyethanol (methyl cellosolve)	21.6%
propan-1-ol	7.5%
propan-2-ol	4.1%
methanol	2.9%

It is clear from these data that 2 methoxyethanol allows a measurable amount of activity, whereas methanol causes a drop of activity to an unrealistically low level.

The relation between solvent concentration and enzyme activity was also investigated, and the result for four solvents is shown in *Figure 2.17.* It should be noted that the curve for 2 methoxyethanol is

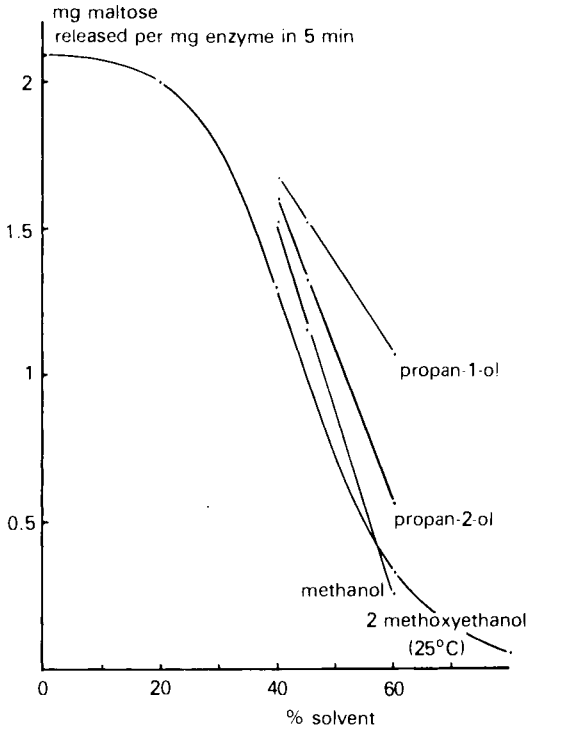

Figure 2.17. The dependence of enzyme activity on solvent centration at 37°C.

derived from experiments done at 25°C; data for the other solvents deriving from reactions at 37°C. The form of all four curves would be expected to resemble that for 2 methoxyethanol if larger ranges of concentration had been investigated for all solvents. The enzyme activity for a given organic solvent is seen to be proportional to the water concentration in the resultant reaction mixture, within the useful range of solvent mixtures (30-60% solvent).

These observations may be explained by the following suggested reaction:

$$\text{enzyme (active)} + \text{solvent} \rightleftharpoons \text{complex (inactive)}$$

The proportion of inactive complex: active enzyme at any one time is determined by the percentage of organic solvent in the mixture, and the activity of the residual non-complexed enzyme at any one solvent concentration is found to be proportional to the enzyme concentration as seen in *Figure 2.18.*

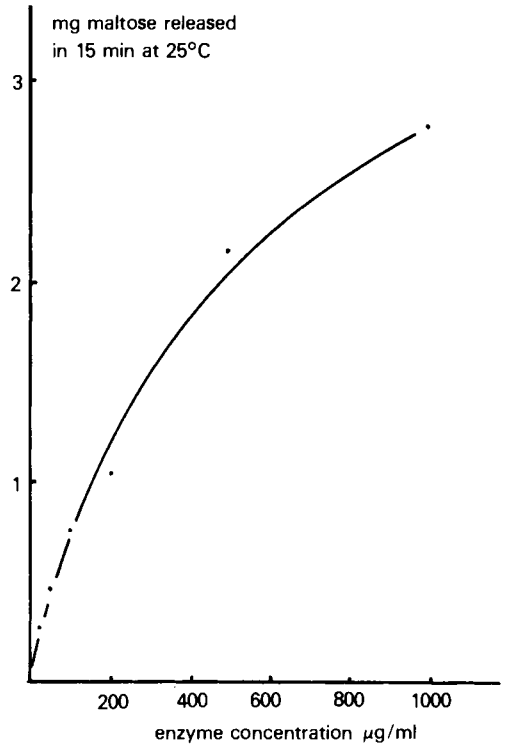

Figure 2.18. Dependence of activity on enzyme concentration in 45% MeOH.

The reversibility of the reaction is demonstrated by the fact that enzyme recovered from the solvent/buffer medium and re-assayed in buffer solution was found to have lost very little of its original activity *Figure 2.19.*

Since the best activity observed in 50% solvent (methyl cellosolve) is only 21.6% of the activity in aqueous buffer, it is obviously necessary to optimize all other conditions if a realistic reaction time is to be obtained.

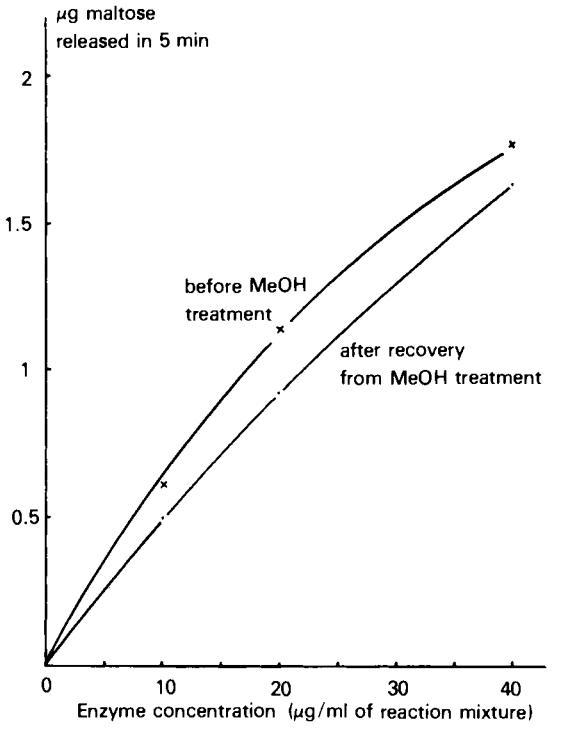

Figure 2.19. Activity of enzyme before and after use in 45% MeOH medium.

The importance of pH is shown by the fact that changing the working pH of α-amylase from pH 7 to pH 7.2 reduced the activity by nearly half. Thus, particularly when working with organic solvents, it is best to use buffers specifically made up to the correct pH for each enzyme, and not the compromise pH which we have found adequate for aqueous work.

The importance of temperature was shown in assays of enzyme activities at 25°C designed to determine whether the inactivation of the enzyme was any less severe at the lower temperature. A wider range of solvents was tested at this temperature, the percentage activities (relative to aqueous buffer) being:

methyl cellosolve	5.8
digol	3.9
diglyme	3.7
dioxane	3.7
propan-2-ol	2.9
1,2 ethandiol	2.9
methanol	2.3
dimethylformamide	1.7

Tetrahydrofuran was also tested but gave unsatisfactory results, probably due to peroxide impurities which interfered with the colour reaction.

As the lower temperature did not seem to protect the enzyme from inactivation by organic solvents, and also produced the added disadvantage of lower reaction rates, all further work was done at 37-40°C.

What has been said above for α-amylase would seem to hold also for protease. The method of enzyme assay in this case had to be carefully chosen, since the organic solvent interfered with some of the usual methods. The method chosen depends upon the production of one N-terminal peptide fragment for each attack by the enzyme on the protein. These fragments react with ninhydrin to form a purple compound which is estimated spectrophotometrically. The procedure was exactly that given by Reimerdes,[6] except that the combined casein substrate and buffer solution (I + II) was in each case diluted with 0.6 ml. of either water or organic solvent as appropriate. The results for two solvents are shown in *Figure 2.20.* The activities relative to that in aqueous solution are:

2 methoxyethanol	3%
propan-2-ol	1.5%

These activities are low, but may be satisfactory for some purposes, for example the removal of surface deposits of glue.

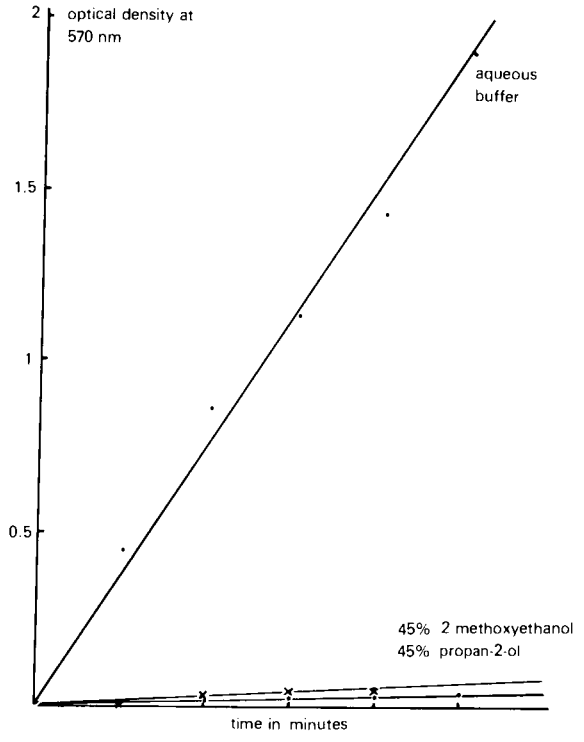

Figure 2.20. The activity of protease in some solvents and in aqueous buffer.

(3) The use of the method on some samples of library materials

225 ml purified water and 50 ml 0.2 M phosphate buffer are warmed to 40°C in a dish in a fume cupboard. A small portion of this is used to dissolve 0.5g. α-amylase (type III A from Sigma Chemical Company). 225 ml. solvent (2 methoxyethanol or propan-2-ol) is added to the warmed buffer followed by the dissolved enzyme. The supported manuscript is immersed in the solution and the dish covered with baking foil to reduce loss of the solvent by evaporation. A small hole is made in the foil for the thermometer. The dish is gently rocked and the temperature maintained at 40°C. The manuscript is examined after about 75% of the estimated reaction time has elapsed, and again at intervals thereafter as may be necessary. When the adhesive is sufficiently broken down, the supported manuscript is rinsed three or four times in cold solvent/water/buffer mixture of the same proportion as the reaction mixture and then well blotted before air drying in the fume cupboard.

The first tests were performed on leaves of a 1548 printed book, almost every page of which had been identically repaired 90 years ago with a slightly oily paper, stuck down with starch paste. The results are summarized in *Table 2.8* (samples 1-6). It should be emphasized that the concept of 'repair starting to lift' is a somewhat vague one, and only approximately quantitative. Within this limitation, however, it can be seen that the order of time of lifting of the repairs is that which would be predicted from the results given in part (2) and the ratios of the times are not too far from what would be expected.

It will be seen from *Table 2.7* that printing ink is not completely stable in 45% 2 methoxyethanol. As a result of this, it was difficult to distinguish between, on the one hand, the offsetting of the ink onto the repair (without detachment of fibres of the main sheet), and on the other hand, 'skinning' of the main sheet, transferring the ink image to the repair *with* some of the fibres of the main sheet, the adhesive not having been sufficiently broken down. The times given in this case are probably overestimates resulting from an extra degree of caution.

Subsequently more fragile manuscripts (*Table 2.8,* samples 7-9) were treated using both propan-2-ol and 2 methoxyethanol, and the method was found to work well in all cases tried. Samples of repairs attached with animal glue which could be used to test the use of protease under similar conditions are not plentiful in the authors' library, but a few were tried, and the results here were also very acceptable.

The use of enzymes in these partially non-aqueous solvent mixtures is now the method of choice in the authors' unit for the removal of all repairs and adhesive layers from both printed and manuscript materials, where the inks are fugitive in wholly aqueous solutions.

Table 2.8 Removal of repairs from some early printed and MS pages with α-amylase

Sample	*Repair*	*Solvent*	*Buffer pH 6.9*	*Temp.*	*Repair starting to lift*	*Repair removed*	*Adhesive removed*
1.	Vegetal tissue	water, no enzyme (control)	—	40°C			5 hr. No sign of lifting
2.	Vegetal tissue	water	tris-HCl	39°C	8 min.	45 min. repair floating	2 hr. 30 min.
3.	Vegetal tissue	water	PO_4	39°C	8 min.	45 min. repair floating	2 hr. 30 min.
4.	Vegetal tissue	2 methoxyethanol (45%)	PO_4	31°C	1 hr. 45 min.	2 hr. and 3 hr. samples of repairs	5 hr. 30 min.
5.	Vegetal tissue	2 methoxyethanol (45%)	PO_4	40°C	2 hr.	(Removal after drying)	4 hr. 30 min.
6.	Vegetal tissue	propan-2-ol (45%)	PO_4	40°C	2 hr.	(Removal after drying)	4 hr.
7.	Old paper	2 methoxyethanol (45%)	PO_4	40°C	10 min.	20 min.	40 min.
8.	Old paste only	propan-2-ol (45%)	PO_4	38°C	—	—	35 min.
9.	Old paste only	2 methoxyethanol (45%)	PO_4	38°C	—	—	20 min.

Samples 1-6. Gatherings of book printed in 1548. Repaired in 1890s with 2cm strips of vegetal paper along the head of every page. The paper is very weak and decayed under the old repairs.

Sample 7. Fugitive seventeenth century iron gall ink manuscript on paper, backed with old paper.

Samples 8-9. sixteenth century illuminated music manuscript on paper, with very acid and fugitive iron gall ink. The old silk mesh repairs were removed in alcohol and water, leaving a heavy paste deposit.

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2.1.3 Increase of paper permanence by treatment with liquid ammonia or ammonia solutions: Part 1, Fundamental basis and influence on fibre and paper structure and properties

Adel Koura and *Thomas Krause*

The brittleness of paper as a consequence of natural or accelerated ageing is at least partly due to cross-linking of the cellulose and hemicellulose chains in the fibre walls or in the region of fibre-fibre-bonds.

A treatment with liquid ammonia or with concentrated ammonia solutions should cause changes in the supermolecular structure of the fibre and in effect reduce the area capable of cross-linking or break already formed crosslinks.

Test sheets made from bleached wood pulp were treated with liquid ammonia at — 50°C resp. with 55 to 75% solutions at —20°C, before and after accelerated ageing at 90°C and 70% RH. The folding endurance of pretreated test strips declines to a very much lesser degree than that of untreated specimens. Ammonia treatment after accelerated ageing causes significant increase in the folding endurance and the brightness. In both cases the properties of the paper in respect to 'usability' were significantly improved by the ammonia treatment.

To understand the nature of changes brought about by liquid ammonia and ammonia solution treatment of paper, it is essential to know the morphology and the fine structure of the fibres as well as the mechanism of paper ageing. *Figure 2.2.1* shows the schematic structure of the fibre in unaged and aged state. Paper fibres consist mainly of cellulosic fibrils but in addition contain varying amounts of hemicelluloses. Analysis of cellulose fibres by X-ray diffraction has shown that the constituent molecules exist in definite patterns in certain regions of the fibre, referred to as the crystalline regions. In other regions, however, the molecular arrangement is more random and less compact and these are referred to as the amorphous areas. Amorphous areas vary from regions of complete randomness to regions with limited order. All these structural differences are of important effect on the reactivity and the physical properties of cellulose fibres. By beating, during which the cellulose fibres are cut, bruised and fibrillated, the external and internal surfaces of the fibres increase enormously and this results in an improvement of the strength of properties of paper.

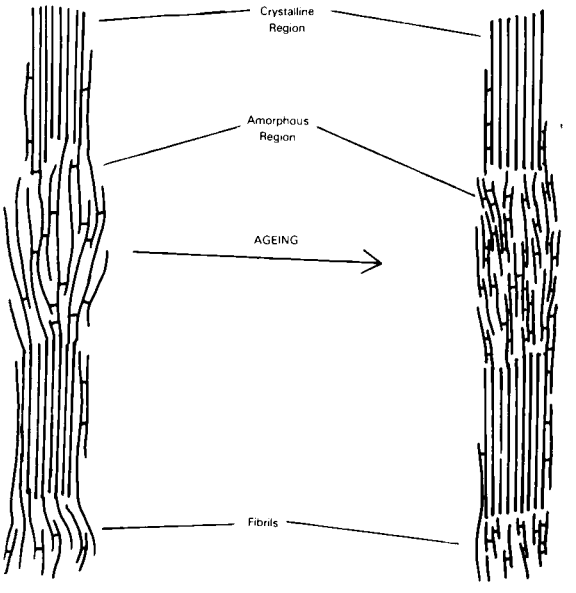

Figure 2.21. Schematic representation of the elementary fibril of cellulose to illustrate the ageing mechanism.

A number of articles have been written about the ageing mechanism of paper, describing reactions of cellulose during the ageing process. Hydrolysis, oxidation, cross-linking and changes in lateral order or crystallinity are possible reactions during the natural ageing of paper. In addition, thermal decomposition must be considered during accelerated ageing. Hydrolysis, oxidation and cross-linking would occur in the fibrewalls as well as in the fibre bonding areas. The hemicelluloses are much more readily accessible. Because the hemicelluloses are in the amorphous regions, their rate of degradation and cross-linking will be much greater than that of cellulose.

Hydrolysis causes a decrease in the chain length of the cellulosic polymers by random breaking of the chains in the amorphous regions. Excessive chain shortening results in a gradual decrease of fibre and paper strength. Oxidation increases the carbonyl and carboxyl content, followed by a decrease in brightness. The increase in wet strength and the strong decrease in folding endurance by ageing shows that cross-linking reactions are occurring and this aspect shouuld be incorporated into any theory of paper ageing and permanence. The lower humidity content of aged papers, predominantly a result of dehydration, indicates that water molecules firmly held between the cellulose molecules have been released, allowing the formation of more stronger hydrogen bonds within the existing bonded areas or that of intermolecular hemi-acetal or ether linkages as suggested by Back. These changes in lateral order of cellulosic fibres will affect most physical properties of paper, especially its flexibility.

To break up the lateral bonds formed during ageing or to prevent the formation of these bonds, it is necessary to change the morphological structure of the fibres. One method is the treatment of the cellulosic fibres with swelling agents. Most swelling agents, such as concentrated solutions of caustic soda, dissolve great parts of the fibrous material and destroy the paper structure. Anhydrous ammonia, on the other hand, penetrates cellulose easily and reacts with the hydroxyl groups after breaking the hydrogen bonds, without practically dissolving any cellulosic or hemicellulosic material. The reaction presumably occurs in the less-ordered (amorphous) region as well as in the cyrstalline regions. The basic attraction of liquid ammonia is its rapid and uniform reaction and the possibility of its ready elimination. Structural changes, corresponding to those experienced with liquid ammonia, can also be obtained by treatment with 50-60% ammonia solutions.

It was found that treatment of natural and accelerated aged paper with liquid ammonia or ammonia solutions of high concentration (above 55%) resulted in a considerable reduction of brittleness measured as increase in folding endurance and therefore improves their performance.

Different processing parameters used during ammonia treatment such as ammonia concentration, contact time, method of ammonia elimination were investigated. It was found that the time of soaking in liquid ammonia or ammonia solution is not critical to reach the maximum effect. The time of soaking can be limited to a few seconds. Further it was found that the higher the ammonia concentration, the better the effect on durability. Practically no differences were observed between the ageing resistance of papers from which ammonia was removed by evaporation and those from which the ammonia was removed by cold or hot water washing and additional drying. Finally we concluded that the most effective method was to remove the ammonia from the treated paper is by evaporation. The air-dried paper was then rewetted with water and smoothed in the drier under pressure.

Some mechanical properties of papers treated

Table 2.9. Some mechanical properties of ammonia-treated paper

Sample	*Dry tensile strength (N)*	*Wet tensile strength (N)*	*Folding endurance after 10 days accelerated ageing (1000 g tension load)*
Untreated paper	87.1	1.03	170
Liquid ammonia treated paper	52.9	3.96	1200
Ammonia solution (65%) treated paper	87.2	6.4	900

(N = Newtons)

with liquid ammonia and ammonia solution in comparison with untreated paper are summarized in *Table 2.9.* Treatment with liquid ammonia resulted in a considerable reduction of dry tensile strength. However, after treatment with ammonia solutions the tensile strength remained about the same as for the untreated control paper. Liquid ammonia or ammonia solution treatment produced a paper with higher wet tensile strength than that of the untreated paper. Treated papers after 10 days' ageing at 90°C and 70% r.h. showed a much higher folding endurance than the untreated control samples.

Table 2.10 shows that liquid ammonia or ammonia solution treatment causes higher opacity and lower density compared with untreated paper. The treatment also resulted in a considerable increase of the paper thickness and roughness. Brightness after 10 days' ageing and brightness stability is much better than that of the untreated sample. The water retention value of the fibres decreased as a consequence of the treatment, due to irreversible hornification in the fibre walls. It is evident that treatment with liquid ammonia is superior in increasing the ageing resistance compared with ammonia solutions.

Table 2.10 Some physical properties of ammonia-treated paper

Sample	*Opacity*	*Density g/cm³*	*Thickness mm*	*Roughness ml/min*[a]	*Brightness after 10 days' accelerated ageing*	*WRV*[b] *%*
Untreated paper	67.4	0.7189	0.114	409	54	110
Liquid ammonia treated paper	78.4	0.5743	0.152	751	68	52
Ammonia solution (65%) treated paper	71.0	0.6643	0.133	634	65,5	62

[a] Roughness ml/mm refers to a standard procedure used in the paper industry.
[b] WRV = water-retention value.

Table 2.11. The effect of ammonia treatment on papers containing groundwood on the folding endurance

Sample	*Folding endurance after 10 days' accelerated ageing*		
	Untreated	*Liquid ammonia treated*	
		before ageing	*after ageing*
100% groundwood[a]	40	70	114
80% groundwood[a] 20% sulphate pulp[b]	50	105	156
50% groundwood[c] 50% sulphate pulp[c]	90	707	162
100% sulphate pulp[d]	170	1200	500

[a] Measured by 200 g tension load.
[b] Measured by 500 g tension load.
[c] Measured by 700 g tension load.
[d] Measured by 1000 g tension load.

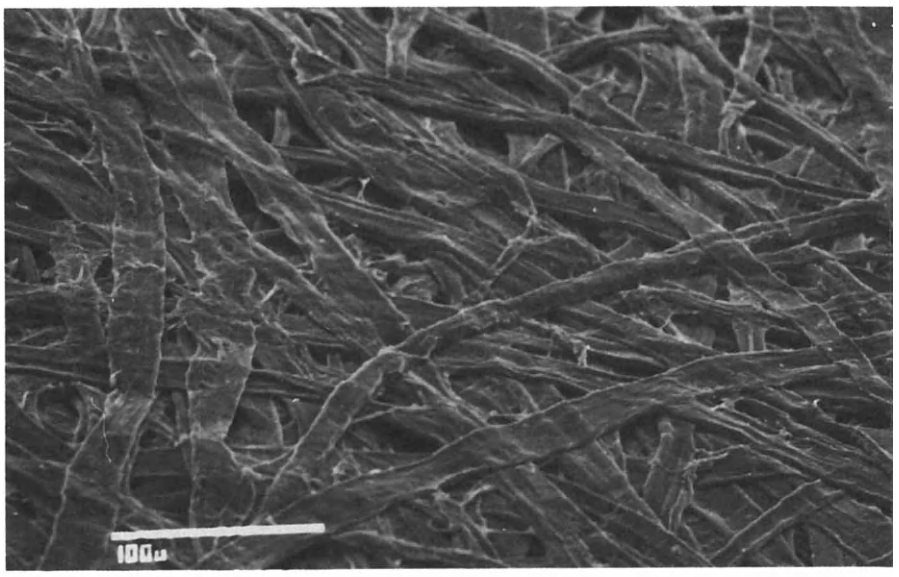

Figure 2.22(a). View of the surface of untreated paper (enlargement 300 ×).

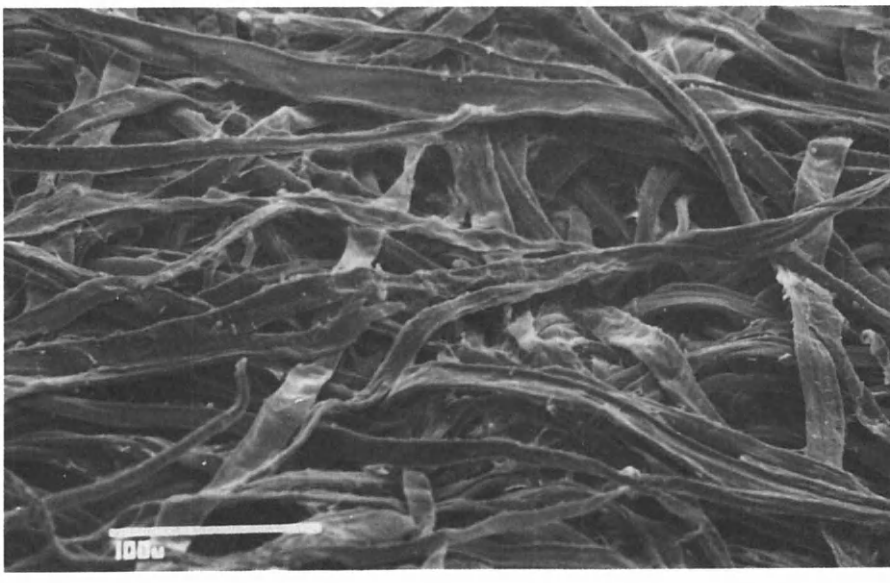

Figure 2.22(b). View of the surface of ammonia treated and air dried paper (enlargement 300 ×).

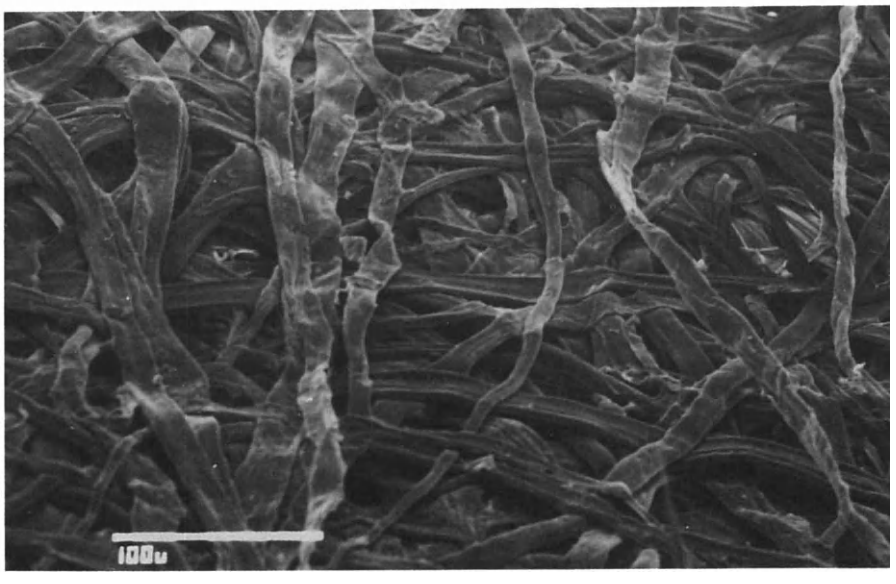

Figure 2.22(c). View of the surface of ammonia treated paper air dried, rewetted and dried under pressure (enlargement 300 ×).

It was also found that treatment of groundwood containing papers with liquid ammonia or ammonia solutions strongly increased its ageing resistance measured as folding endurance after accelerated ageing. *Table 2.11* shows the effect of ammonia treatment on such papers containing different ratios of chemical wood pulp. The ammonia treatment improves not only the ageing resistance but also increases the folding endurance of already aged papers. These effects decrease with increasing groundwood content.

Another advantage of ammonia treatment is the neutralization of acidity in papers and the removal of some materials such as sizing agents which reduce generally the ageing resistance.

In addition, ammonia treatment of aged paper increases its brightness, a small part of degradation products being dissolved which are responsible for yellowing of the aged paper.

Scanning electron micrographs of the surface of treated and untreated papers are shown in *Figure 2.22* (a, b and c). The observations are in correlation with the changes in paper properties after treatment with ammonia, i.e. lower density, higher roughness, increasing sheet thickness and high opacity.

The following schematic picture *(Figure 2.23)* illustrates the effect of liquid ammonia and ammonia solution treatment. The untreated fibres tend to collapse and therefore result in high density sheet with low opacity and low roughness. Ammonia-swollen fibres have more or less rounded cross-sections, therefore the sheet has smaller fibre-to-fibre bonding areas, low density, high opacity and high roughness. There will be more and longer unbonded fibre segments and as a consequence the sheet will become much more flexible. These changes in sheet structure appear to survive to a great extent, even if the sheet is air-dried, rewetted and smoothed.

The real chance of increasing the ageing resistance by renewing age-damaged paper materials through ammonia treatment, as we see it, lies in the development of an automatically or at least semi-automatically working process. If this process is combined with a succeeding polymer impregnation the paper's mechanical and optical properties should be retained even after 10 days' artificial ageing as described above. It surely will be a long and expensive way up to the day when this process can be proved in action, not only in the laboratory, but in the archive or in the library, but there is good reason to be optimistic.

Acknowledgements

The authors would like to thank the Volkswagen Foundation for financial support.

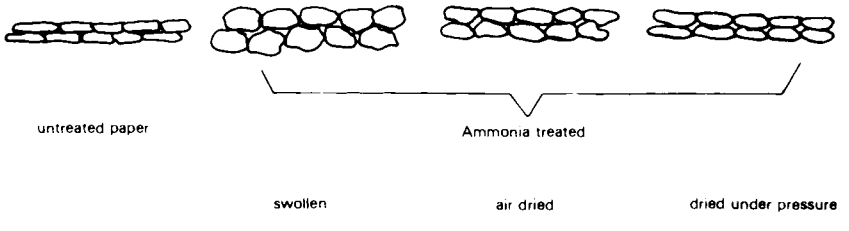

Figure 2.23. Schematic representation of the paper cross section to illustrate the effect of ammonia treatment on the paper structure.

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Editor's note

It perhaps should be emphasized that the changes in the properties of paper described in this paper are only observed when the concentration of ammonia in the liquid phase is greater than 55%. Treatment with gaseous ammonia or dilute solutions cannot cause the observed effects, which are not a result of deacidification by the ammonia, although this, of course, happens also.

2.1.4 Increase of paper permanence by treatment with liquid ammonia or ammonia solutions: Part 2, The influence of treatment with liquid ammonia or ammonia solutions on the permanence of inks

Wilfried Feindt

A range of samples of record papers with written and printed texts ranging from the late sixteenth century to the present day were treated with liquid ammonia and ammonia solutions. The reactions of both the papers and the inks and printing colours were investigated and recorded. A list of colours and their response to these treatments is presented. It shows that certain categories of books and records can be treated by these methods without risk of damaging print or writing.

Introduction

The starting point of the quest for a technique bringing about a betterment of the ageing properties of paper was a research programme arranged by the Lower Saxon State Archives at Bückeburg, the Cellulose and Paper Chemistry Sections of the Institute for Macromolecular Chemistry of the Technical University of Darmstadt, the Institute for Book Restoration at the Bavarian State Library at Munich and the Duke August Library at Wolfenbüttel. The investigations, which are financed by the Volkswagen Foundation, are intended to find restoration methods for papers containing ground wood and to ascertain the influence of aqueous restoration methods and the effect of defined bleaching techniques with respect to the ageing resistance of paper.

In the quest for appropriate restoration techniques for papers containing ground wood Professor Dr. Th. Krause and Dr. A. Koura, both of the Technical University of Darmstadt achieved a first success within a short time. By the technique of the treatment of cellulose with liquid ammonia — a technique borrowed from textile finishing — the ageing resistance of paper can be very much improved. This knowledge was obtained by laboratory experiments with blank papers of different types and properties. It is true that the technique proved to be not very effective for the treatment of papers containing pure ground wood. Equally, no improvement was obtained with paper which was already very brittle regardless of its fibre content.

Nevertheless there are a number of applications in the restoration workshop resulting from the development of this technique. The improvement of the mechanical properties and the ageing resistance of paper can be exploited in the workshop, however, only if the following factors have been considered.

(1) The technique which has been developed to date has only concerned blank papers and is appropriate for the restoration of paper artifacts in libraries and archives only if it does not ruin the printing and writing materials or change them substantially. This question will be dealt with below.

(2) Taking into account the quality of paper in such repositories which requires treatment, the technique must be appropriate for mass restoration.

Investigation materials, investigation conditions, conditions of testing

In order to find out the effect of the technique on inks, Indian inks, printer's colours, pencils and

other writing materials a considerable number of test samples were used:

(1) Iron-gall inks on record leaves dated 1567-1928.
(2) Printers' colours on printings dated 1794-1980.
(3) Inks, stamp inks, pencils, coloured pencils, typewriter ribbons, reprint colours in record leaves dated 1903-1958.
(4) Inks and ball-point pen media, with which the test papers were inscribed.

These writing materials were obtained partly by firms selling office supplies and partly they were made available in a finished condition by the firm Mittenwald-Chemistry. Finally inks were produced from dyestuff samples produced by BASF and Farwerke Hoechst[1]. Further details can be seen in *Table 2.12*.

Strips c. 1.5 × 18 cm were cut out of the test leaves as test samples.

Some of the samples were treated in ammonia, which had been cooled to −45° to −50°C, with a water content of 15%. The treatment took 2 minutes. Later on the samples were put in a fume cupboard so that the ammonia could evapoate. After evaporation the dry samples were placed in a double-boiler and on a Rapid-Köthen-apparatus under heat and vacuum dried and glazed.

For the writing materials, which are sensitive to water, the treatment was altered. The samples were treated 2 minutes in pure ammonia without addition of water. In order to glaze them, the evaporated samples were sprinkled with a little water and dried on the Rapid-Köthen-apparatus. Glazing tests without water were not successful with either method of treatment.

After the treatment random measurements of the dimensional changes of the papers were taken. They had shrunk by an average of about 5%, handmade rag papers generally less, modern machine-produced papers more.

Unfortunately the thickness increase could not be measured. The reaction of the writing materials was judged only visually. The results are presented in *Table 2.12*.

Discussion of the results

The tested printers' colours remained unaltered, though the deep-frozen solution of ammonia contained water and water also was used for the process of washing and glazing. Problems only arose with strongly coated paper, from which the coat partly scaled off. With these minor reservations the technique should be applicable for printed works in library restoration workshops.

Also iron-gall inks of different chronologies did not alter by this treatment in spite of the water. Only a modern iron-gall ink, to which was added a blue dyestuff in order to show the writing quickly, altered colour by the treatment.

Black reprint colour, typewriter carbon, pencil, blue pencil and the greater part of the tested ball-point pen media were not in the slightest dissolved. The ball-point pen pastes had been those which are permissible for use on official documents according to DIN 16554.

Many modern dyestuff inks, which are used in fountain pens and fibrous pens, turned out to be problematical. The alterations range from a little bleeding of the colour through a nearly complete smearing of the letters writing to entire disappearance. Many stamp inks, reprint inks and coloured pencils reacted in like manner. Some of them dissolved in liquid ammonia, with others the colour was dissolved by the water needed for the glazing.

As far as archives are concerned, these results mean a limitation in the range of applications of the technique. In the conservation treatment of modern records it would be necessary to first fix the soluble dyestuffs. But if one searches systematically, one should succeed in finding an appropriate polymer for this purpose. In fact, we have probably found the first one, an acrylic polymer. A solution of 4% Plexisol p550 (produced by Röhm, Damstadt) in benzol preserves the writing. The film is impermeable to NH_3molecules.

Prospect

The technique of the treatment of paper with liquid ammonia and solutions of ammonia is suited (with certain reservations) to application in restoration workshops. Printers' colours and iron-gall inks seem to be stable, other modern writing materials only partially so.

Therefore such treatment would cause less problems with library material than with the archives.

The alteration of the size of the treated papers — as described above, they shrink at the same time as their caliper (thickness) increases — would force libraries to treat whole volumes. But the improvement in quality carries more weight than the costs which accrue from the disassembling and rebinding

of books. The technique seems suited for mass restoration as well.

The technical conditions for the construction of a machine, which employs this technique, already exists in the textile industry. (Cotton or rayon are mercerized in this way.) The tissue which is to be treated is fed width-wise through the machine.

In a corresponding plant installed in a restoration workshop the paper leaves would have to be transported on a supporting tissue, e.g. on a polyester web. In co-operation with mechanical engineers, the textile finishing industry, the cellulose and paper chemistry and the restoration workshops we intend to initiate the construction of such apparatus.

Note

1. 0.5-2 g dyestuff each of Sudantiefschwarz BB. Viktoriareinblau FBO (BASF), Remastral-Blue 3 G, Amido-Black HTT, Ink-Blue BJTN KZ and Duasyn-Säureblau FBO (Hoechst) were dissolved in 50 ml boiling distilled water, to which were added 10 drops of a preservative (Delegol produced by Bayer), cooled and filled up to 100 ml. Using hydrochloric acid to produce a pH of 2, 0.5 g of dyestuff each of Brilliant-Blaubase SM (Hoechst) and Blaubase KG (BASF) was dissolved in 50 ml of benzyl alcohol.

Table 2.12

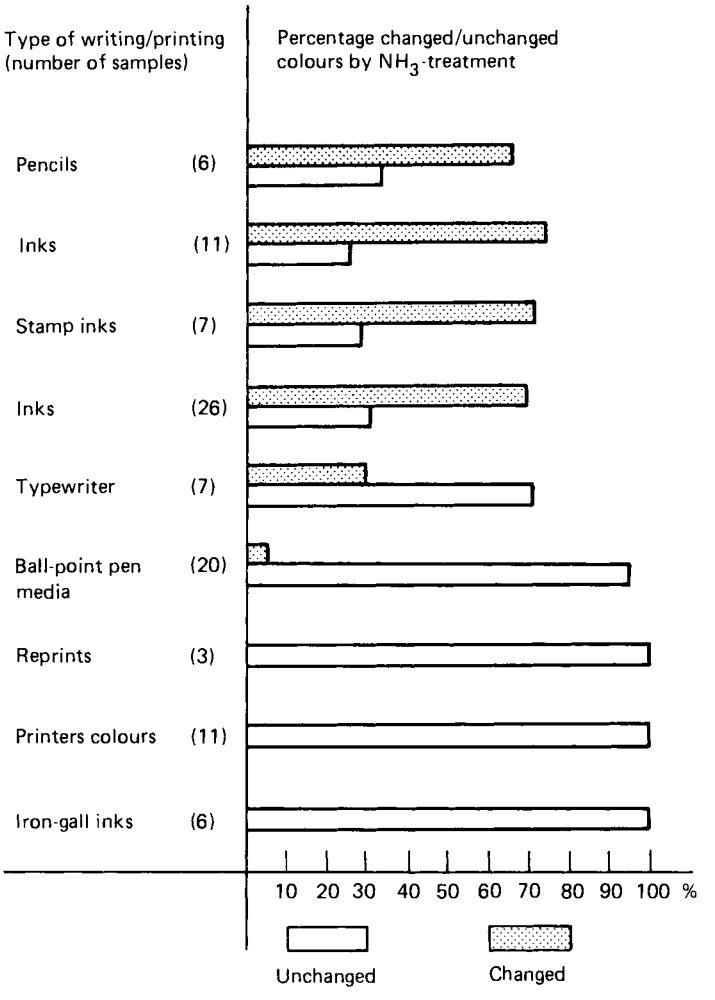
Writing material	Paper	Year	Treatment with $NH_3 + H_2O$	Treatment with NH_3	Alterations in the writing material	Remarks
(1) Iron-gall inks	Rag	1567	+	–	°	—
	Rag	18th Cent	+	–	°	Blue paper decolourized
	Rag	1738	+	–	°	—
	Ground wood	1869	+	–	°	—
	Pulp	1884	+	–	°	—
	Pulp	1928	+	–	°	Blue dyestuff dissolved
(2) Printers colours	Rag	1794	+	–	°	—
	Rag	1810	+	–	°	Dye disappears
	Rag	1838	+	–	°	Blue paper decolourized
	Pulp	1852	+	–	°	—
	Ground wood	1920	+	–	°	Paper becomes yellowish
	Ground wood	1943	+	–	°	Paper brightened
	Ground wood	1968	+	–	°	—
	Ground wood	1974	+	–	°	Strongly coated paper, from which the coat scales off, together with parts of the printers' colour
	Ground wood	1978	+	–	°	Stained printers' colours unaltered
	Ground wood	1980	+	–	°	Newsprint becomes yellowish
	Ground wood	1979	+	–	°	Previously aged 45 days at 90°C at 70% RH
(3) Typewriter	Pulp	1903	–	+	–	—
Carbon	Pulp	1915	–	+	°	—
Typewriter	Ground wood	1918	–	+	°	—
Typewriter	Ground wood	1920	–	+	°	—
Typewriter	Pulp	1928	–	+	°	—
Typewriter	Pulp	1940	–	+	°	—
Typewriter	Ground wood	1950	–	+	–	—
Reprint, violet	Pulp	1903	–	+	°	—
Reprint, violet	Groundwood	1918	–	+	°	Colour weaker
Reprint, black	Ground wood	1935	–	+	°	—
Ink, black	Pulp	1903	–	+	–	—
Ink, blue	Pulp	1906	–	+	– –	—
Ink, black	Pulp	1915	–	+	°	—
Ink, black	Pulp	1914	–	+	– –	—
Ink, blue	Pulp	1917	–	+	– –	—
Ink, blue	Ground wood	1918	–	+	°	—

Writing material	Paper	Year	Treatment with $NH_3 + H_2O$	Treatment with NH_3	Alterations in the writing material	Remarks
Ink, blue	Pulp	1920	–	+	– –	—
Ink, violet	Pulp	1920	–	+	– –	—
Ink, red	Ground wood	1940	–	+	– –	—
Ink, green	Ground wood	1950	–	+	– –	—
Ink, blue	Ground wood	1958	–	+	– –	—
Stamp ink, violet	Pulp	1903	–	+	–	—
violet	Pulp	1915	–	+	°	Colour weaker
blue	Pulp	1917	–	+	–	—
Stamp ink, violet	Pulp	1920	–	+	– –	—
violet	Pulp	1928	–	+	–	—
blue	Pulp	1940	–	+	°	—
blue	Ground wood	1958	–	+	–	—
Pencil	on all papers		–	+	°	—
Blue pencil	on all papers		–	+	°	—
Copying pencil	Pulp	1918	–	+	– –	—
	Pulp	1920	–	+	–	—
Red pencil	Ground wood	1941	–	+	– –	Colour nearly washed out
	Ground wood	1958	–	+	– –	Colour nearly washed out
(4) Inks						
Pelikan 4001 black	Samples written on rag and pulp	1800 1895 1979	–	+	°	—
green			–	+	– – –	—
blue			–	+	– – –	—
markana 30 black			–	+	°	Colour becomes blue
Mittenwald Dokumental						
F 3849 blue			–	+	–	—
LK 6279 blue			–	+	– –	Colour altered
LK 6459 blue			–	+	– –	—
LK 6578 A blue			–	+	–	Colour altered
LK 7011 A blue			–	+	– –	Colour altered
F 3180 black			–	+	– –	Colour altered
F 5011 black			–	+	– –	Colour altered
LK 6185 black			–	+	°	—
LK 6829 black			–	+	–	—
F5030 green			–	+	–	Colour much weakened
LK 6232green			–	+	– –	Colour much weakened
F 5020 red			–	+	– –	Colour altered
LK 6455 red			–	+	– –	Colour altered
LK 6735 red			–	+	– –	Colour altered
BAFS Sudantiefschwarz						
BB			–	+	°	—
Blaubase KG			–	+	°	—
Viktoriareinblau FBO			–	+	°	—
Hoechst Remastral-Blau 3G			–	+	°	Colour a little weaker
Amido-Schwarz HTT	–		–	+	– – –	—
Tintenblau BJTN KZ			–	+	– – –	—
Duasyn-Säureblau VF			–	+	– –	—
Brillant-Blaubase SM			–	–	°	—
Ball-point pen pastes:						
Mittenwald Dokumental						
Type 600 B blue			–	+	°	Little alteration of colour
303/171 B blue			–	+	°	—
303/209 nlue			–	+	°	—
303/400 B blue			–	+	°	—
303/406 B red			–	+	°	Little alteration of colour
red			–	+	°	—
Doku red			–	+	–	Little alteration of colour
303/174 B black			–	+	°	—
303/175 black			–	+	°	—
Doku black			–	+	°	Little alteration of colour

Writing material	Paper	Year	Treatment with $NH_3 + H_2O$	Treatment with NH_3	Alterations in the writing material	Remarks
303/408 B green			–	+	°	Little alteration of colour
Schneider Nr. 7514 green			–	+	°	Colour becomes blue
Nr. 7511 black			–	+	°	—
Rambold Nr. 391 blue			–	+	°	—
Nr. 352 black			–	+	°	—
Bürpactuell Nr. 378 blue			–	+	°	Little alteration of colour
Nr. 387 red			–	+	°	Colour a little weaker
Rotring blue			–	+	°	—
Rempex green			–	+	°	Alteration of colour
Laurin blue			–	+	°	Alteration to colour

° Unaltered
– Little bled
– – Much bled
– – – Completely washed out

Table 2.13



2.15 Increase of paper permanence by treatment with liquid ammonia or ammonia solutions: Part 3, Testing of the *usability* of papers

Helmut Bansa and *Hans-H. Hofer*

A new method of testing paper properties has been developed which takes into consideration the low strength of used (aged) papers. The method enables a statistically definite description of the properties of paper in respect to its usuage (so called 'Benutzbarkeitsqualität'). The test is suitable for the documentation of the success of any restoration process with papers in archives and libraries.

Test data are reported of papers that were treated with liquid ammonia or ammonia solutions. The measurements allow an estimation of this new method.

A number of methods exist for the testing of newly manufactured papers. Most of them have been developed by the paper industry or by research institutes related to it. Such tests are, for instance: tensile strength, bursting strength and folding endurance. These tests usually deal with very strong papers and give poor results on already weak papers such as some archive materials. It is well known that the results found with these instruments can be misleading, e.g. the measurement of the folding endurance with the MIT tester and similar instruments, since paper with a folding endurance of 'zero' often can be used in archives or in a library without special care. In cases like this, when the MIT fold endurance tester gives a 'zero' result there is no indication of differentiation in quality of the papers, so that the results do not really reveal anything about the comparative *usability* of weak and/or aged papers. Therefore a better test has been looked for, especially to describe the *usability* of aged papers.

The term *usability* is not well defined. Customarily, the mechanical characteristics of aged papers are indicated by such terms as *high strength, poor strength, medium quality,* etc. Such criteria were used to rank 19 selected papers of very different quality, which were arranged according to increasing quality by comparison two by two. Thus a ranking was obtained of the 19 papers beginning with Number 1 for the best and ending with Number 19 for the poorest quality. This was done by librarians and restorers of the Baverische Staatsbibliothek, Munich, and was statistically proofed by calculating Kendall's rank correlation coefficient. [1, 2] For the further steps of this work this ranking was called *usability* and regarded as the standard. Then systems of measurements had to be looked at for corresponding to it as far as possible.

The measuring methods taken into consideration are listed below and discussed later:

(1) Folding endurance according to Schopper[3, 6].
(2) Tensile strength after pressure folding according to Brecht-Wesp[4].
(3) Fatigue bending test according to Schopper[5, 6].
(4) Tensile strength[7].
(5) Tensile strength after *one* defined fold[8].

(1) Folding endurance test results can be correlated according to Schopper with those

Table 2.14. Ranking of the 19 papers by different tests. (No. 1 means best quality, No. 19 worst quality in this collection. Same numbers identify same quality of the papers).

S* compared with line 2 - *usability*. The closer the value to 1, the better the correlation.
n.m. = not measurable.

1. Paper No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	S*
2. Usability	4	3	7	2	15	1	12	14	11	8,5	8,5	18,5	18,5	17	16	13	10	6	5	2 -3 0,8263
3. Folding endurance (Schopper)	2	1	5	3	12	n.m.	10	10	6	n.m.	7,5	15	15	15	15	10	15	4	7,5	2 - 4 0,7338
4. Tensile strength after pressure folding (Brecht-Wesp)	1	2	14,5	3	8	5	11	10	9	n.m.	7	14,5	14,5	14,5	14,5	n.m.	14,5	6	4	2 - 5 0,8807
5. Duration bending (Schopper)	1,5	1,5	11	3,5	10	3,5	9	12	13	6,5	5	19	18	17	14	16	15	8	6,5	2 - 6 0,7952
6. Tensile strength	1	1,5	11	5	17	7	9	15	14	4	8	16	18,5	12	13	10	18,5	6	1,5	2 - 7 0,9132
7. Tensile strength after one defined fold	1,5	1,5	10	3	16	6	11,5	11,5	9	4	8	18,5	18,5	17	14,5	13	14,5	7	5	

Table 2.15. Connection of the measurement of the tensile strength after one defined fold with the *usability*.

		Usability		After one defined fold	
Class	Description	Ranking No.	Paper-sample No.	Tensile strength F [N]	Paper-sample No.
I	*Very firm*	1-4	1, 2, 4, 6	>36 MD or CD	1, 2, 4
II	*Firm*	5-7	3, 18, 19	>12 MD + CD	6, 9, 10, 11, 18, 19
III	*Usable without restriction*	8-10	10, 11, 17	>12 MD or CD	3, 7, 8
IV	*Quite useful*	11-13	9, 7, 16	>4 MD + CD	15, 16, 17
V	*Usable with caution*	14-16	8, 5, 15	>4 MD or CD	5
VI	*Endangered*	17	14	Measurable MD + CD	14
VII	*Not usable anymore*	18, 19	12, 13	Not measurable	12, 13

MD = machine direction.
CD = cross direction.

obtained by the MIT tester. The results of this test did not give any correlation with the *usability* ranking described above.

(2) Pressure folding according to Brecht-Wesp and measurement of the tensile strength after this folding gave reasonable correlation with the *usability* of the papers, but with two serious drawbacks:
(a) For the measurements with the Brecht-Wesp instrument paper-strips with a length of at least 16 cm are necessary. Such samples are often not very easy to obtain from old books;
(b) The instrument is no longer produced and it will therefore be very expensive.

Table 2.16. Treatment of some samples by Krause and Koura with a 80% aqueous solution of Ammonia at 40°C for 2 minutes. The values give the tensile strength in N after one defined fold and the corresponding classification.

Paper No.	1	2	4	7	11	14	16
Untreated sample							
MD	67,9	69,0	38,1	19,7	28,7	1,4	12,1
CD	44,1	32,6	26,2	9,5	16,2	2,5	8,4
Classification	I	I	I	III	II	VI	IV
Treated samples							
MD	70,5	60,0	40,0	19,8	28,5	7,9	20,9
CD	29,6	29,8	27,2	14,5	14,5	6,6	10,3
Classification	I	I	I	II	II	IV	III

(3) The fatigue bending test according to Schopper also gave a reasonable correlation with the *usability* of the papers. The difficulties in measuring this value are that it uses up lots of paper and also measuring time due to variations in the results, even when measurement is done in a simplified manner. In the experiments the bending angle was set to 30 degrees and increased the pulling force in steps from 0,49 N to 2,943 N, to 7,848 N, to 14,715 N.

(4) Measuring the tensile strength and comparing it with the *usability* of the papers gave a reasonable correlation. This fact is clearly understandable especially with strong papers. Here the strength seems to become the dominant factor influencing *usability*.

(5) After these results it was expected that a combination of measurements which determine the tensile strength and the folding or bending behaviour would produce the best result.[9] After the first manual tests an apparatus was constructed which permitted the folding of paper strips with a length of 100 mm and a width of 15 mm once in the middle of their length and under defined conditions. This is carried out using a metal roll with a diameter of 46 mm and a weight of 4,91 N rolling across the paper loop on an inclined plane, with an angle of 20 degrees to the horizontal plane. These results in a force of 4,25 N or a linear pressure of 283,19 N/m, which folds the paper in always the same manner (see Figs. 2.24(a)-(c)).

After folding the paper strips this way their tensile strength is measured.

In *Table 2.14* comparison of lines 2 and 7 shows that this testing procedure really gives the best correlation of all tests, which also shows up by comparing Spearman's rank correlation coefficients with a value $S = 0{,}9132$.[2]

This test therefore is preferable to others for several reasons:

(1) It gives the best correlation with the *usability* scale.
(2) The apparatus is simple and can be built easily
(3) It does not need large amounts of test paper
(4) It is a fast test procedure

To make this test more convenient, a general description of *usability* was developed and a connection with the results of the measurements. A classification of 7 qualities from *very firm* to *not usable anymore* was set up, as laid out in *Table 2.15* with the corresponding results of the measurement of the tensile strength after one defined fold as described above. In this classification only the papers No. 8 and 9 miss their corresponding class of quality by more than one number: by this system of measurement paper No. 9 is lifted from class IV to class II and paper No. 8 from class V to class III. Actually, both papers were made from wood pulp in 1893, but subsequently experienced different

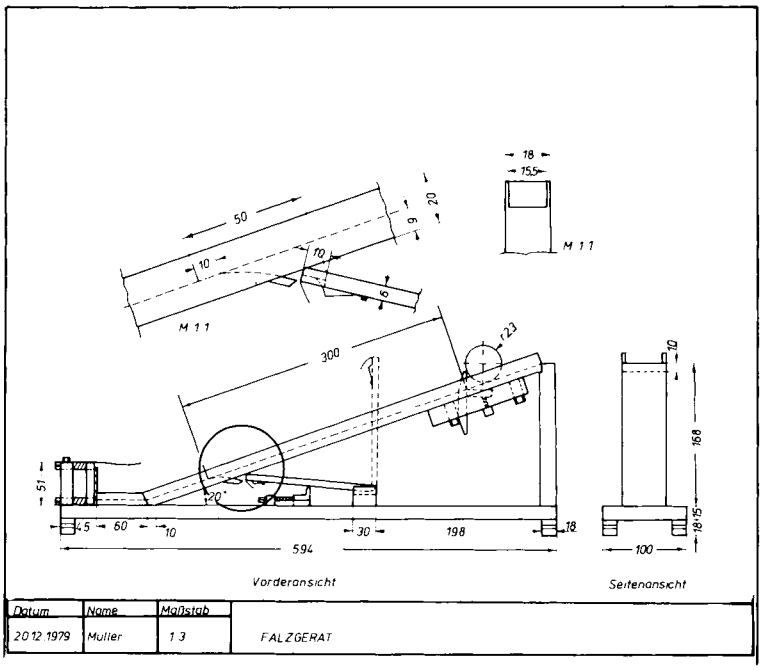


Fig. 2.24(a). Drawing of the folding apparatus for the defined folding of paper-strips. All measures are in millimetres (mm).

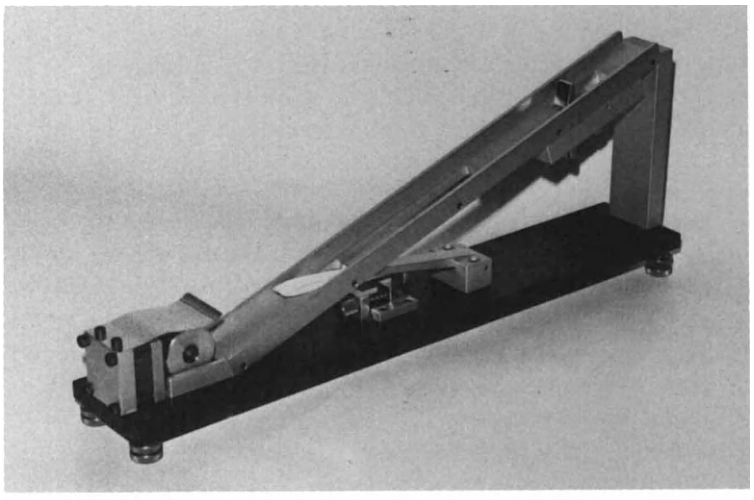


Fig. 2.24(b). Folding apparatus with the folding roll in front of the paper-strip.

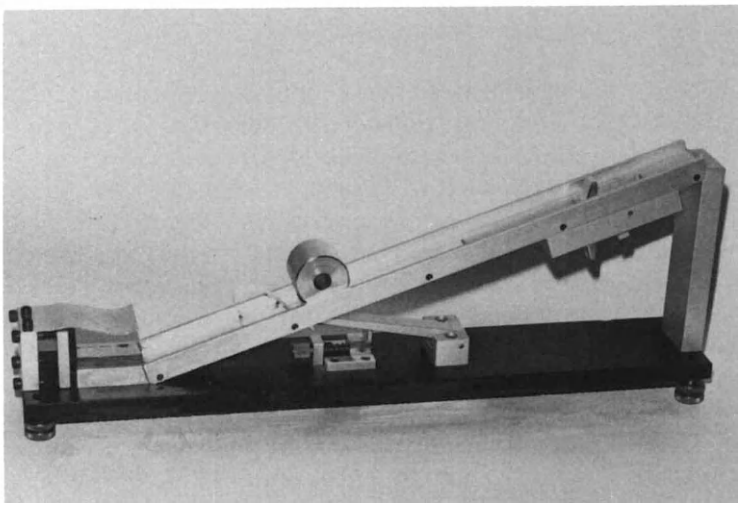


Fig. 2.24(c). Folding apparatus after one fold.

storage conditions. No. 9 was stored in a cool place and not used. It may well be that the restorers testing them gave a lower grade because of their wood content and yellowness. This colouring exists on outer parts of the leaves, whereas for the mechanical tests the inner parts were used. All the other papers are within ± one class in both systems of classification. It is therefore recommended that this classification be use used in the context of weak and aged papers in archives and libraries.

Krause and Koura have stated, in their paper to this conference, that the treatment of papers with highly concentrated ammonia-solutions increases the stability of papers. These researchers also treated some of the papers of this study (see *Table 2.16* for the results).

The already strong papers of class I and II do not show a strong influence by the ammonia treatment, but the weak papers give promising results:

Paper No. 14 goes from class VI to IV; that means from *endangered* to *quite useful.*

Paper No. 16 goes from class IV to III; *quite useful* to *useful without restriction.*

Paper No. 7 goes from class III to II; *useful without restriction* to *firm.*

It is hoped that these results will illustrate the value of our method in determining the *usability* of papers as well as the effect of the ammonia-treatment of brittle papers suggested by Krause and Koura.

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2.2

Conservation Treatments

2.2.1 Alternatives to conventional methods of reducing discolouration in works of art on paper

Keiko Mizushima Keyes

Chemical bleaching has a detrimental effect on paper and conservators are quite concerned with the continued use of conventional chemical bleaching methods. This presentation is concerned with a search for alternative methods which would keep the use of chemical bleaching to a minimum, and eventually may make it possible to dispense with much of our worry.

Paper tends to retain what it absorbs. Therefore, materials used to reduce discolouration of paper should ideally be harmless and not shorten its life. Magnesium bicarbonate, calcium hydroxide and ammonia adjust the pH of wash water to a higher alkalinity and aid releasing discolouration more effectively. Alcohols may be used as wetting agents for highly sized paper. Enzymes have a cleansing action. A vacuum suction table effectively draws dissolved substances out of the paper structure. Sunlight in the presence of moisture and magnesium bicarbonate may prove to be a safer, effective bleaching method, and further studies should be made of bleaching with alternative light sources.

Until recently, hardly anyone questioned the use of chemical bleaching as a standard procedure in the restorative treatment of paper objects. But today, as a result of having better information about the potential degrading effect of chemical bleaching in its immediate and latent actions on paper, the prevailing attitude among paper conservators is cautious and we tend to avoid the use of chemical bleaching in our work as much as possible. However, conservators of works of art on paper are concerned with improving the visual effect of a damaged object in addition to enhancing its physical strength and longevity. If the object is disfigured by discolouration, an attempt is made to reduce it through treatment to regain the visual coherence without which the art object falls short of the meaning it conveys. One challenge posed in treatment of works of art on paper is how to achieve an effective reduction of discolouration by the safest possible means, minimizing the use of potentially dangerous chemical bleaching agents. The purpose of this paper is to discuss some methods which may meet this challenge.

Standard procedure in the treatment of a discoloured object is first to employ dry cleaning methods such as brushing and erasures, and the application of some organic solvents which are safe to the paper and the media. When carried out with skill and ingenuity, these methods can considerably reduce certain stains and surface soil. The materials and methods for dry cleaning are discussed in various publications[1-3]. However, reduction of general discolourations in paper depends on the cleansing action of water. Water cleanses acidity, discolouration and degradation products from paper and strengthens its structure by re-establishing bonding among fibres. Recent findings at the Library of Congress[4] caution about the weakening effect of deionized and distilled water on paper. But the effect of water as a benign solvent for discolourations in paper is generally agreed upon.

Occasionally, chemical bleaches are resorted to prematurely when the effective limit of water's cleansing action seems to have been reached. But

there are safe methods by which the cleansing action of water may be made more effective, and beyond this point there are still safe alternatives for the reduction of discolouration besides chemical bleaching. This paper presents three safe methods of increasing the effectiveness of water as a cleaning agent and an organic alternative to chemical bleaching which is effective in certain instances. This is followed by observations on a traditional technique of bleaching without the use of harmful chemicals.

The use of safe alkaline substances in water cleansing

Since many of the discolourations in paper are acidic in nature, their reduction is achieved most effectively if the water used for the purpose is alkaline. Hey[5] noted that a deacidification procedure removes considerable discolouration from paper. She used solutions of calcium hydroxide and magnesium bicarbonate as immersion baths for this procedure.

The alkaline wash should follow a preliminary plain water wash in most cases to lessen the risk of shock to the paper. Paper conservators have observed that deacidification agents sometimes affect colours and binding of certain media, and occasionally leave a white crystalline deposit of carbonates that cloud the image surface. In cases where it is unsuitable to use a standard solution[6] of a deacidification agent, it should be used diluted in order to avoid these ill effects. Some reduction of paper discolourations can be achieved with a considerably diluted solution (e.g. magnesium bicarbonate to water 1:5, calcium hydroxide to water 1:10) used as an immersion bath. This is perhaps more effective in two baths with air-drying between each immersion. In view of the findings from the research at the Library of Congress[7], it is also important for conservators using deionized or distilled water to add a small quantity of either a calcium or a magnesium compound to their wash water, which will prevent the over-purified water from weakening paper and may increase its effectiveness as a cleansing agent through its mild alkalinity.

Ammonium hydroxide is a weak, volatile alkali, and its salts are soluble in water. Used in weak concentrations, it is considered harmless to paper. Paper washed in water containing a small amount of ammonium hydroxide (droplets of a concentrated NH_4OH, or less than 0.05% of the volume of the wash water) normally looks brighter than paper washed in diluted deacidification solutions.

The same, safe alkaline substances can be used for local applications to discoloured areas such as foxing marks, mat burn and other stains which respond to alkalinity. In local applications, the standard solution of magnesium bicarbonate and calcium hydroxide can be used, and a slightly stronger concentration of ammonium hydroxide solution (e.g. twice the amount used for general washing) can be employed, brushed on to discoloured areas a few times in succession. Additional moisture is then used to flood the area and the released discolouration is leached away with blotting paper or a vacuum suction table (see below). The released discolouration can also be washed away in an immersion bath, but this method of local application is especially useful for objects that cannot be exposed to excess moisture.

A word of caution about groundwood paper. It darkens in alkaline water, and although its acidity is more efficiently reduced by these alkaline substances, its brightness is not enhanced.

The use of alcohols in water cleansing

Among various wetting agents available for our use in the treatment of works of art on paper, alcohols appear to be the safest and most generally applicable to objects. Although alkaline water penetrates into the paper structure better than plain water, highly sized papers, especially those sized with alum rosin, and areas in paper with certain water-repellent stains will often refuse to wet thoroughly. By brushing or spraying an alcohol on the paper, or by mixing some amount in the water, the paper readily allows water to penetrate into its structure, and the cleansing effect of water is enhanced as a result.

Alcohol is particularly useful as a wetting agent when an object is cleansed by flotation over a water bath so long as no friable medium will dislodge and no colour will suffer ill effects from the more effective penetration of water.

Alcohol can be mixed in the water which is applied to discoloured areas of an object that does not allow an excess use of moisture. It helps to prevent the formation of tide marks, and aids in the more effective release of discolouration as well as in faster drying of the areas.

The most common alcohol used as a wetting agent is ethanol. Methanol is more powerful and quicker in its action than other alcohols and is used in situations where such properties are called for as long as it is safe to the object.

The use of vacuum suction table in cleansing procedures

The vacuum suction table, which was introduced by Marilyn Weidner in 1974[8], greatly extended the range of possible treatment of paper objects. Vacuum suction tables are particularly valuable in

the removal of discolouration because of their capacity to evacuate solubilized matters efficiently out of paper without immersion in a water bath, allowing water or organic solvents to flow through the paper structure by the draw caused by the vacuum suction. They are also useful in localizing moisture and solvents to areas under treatment without affecting other areas with fugitive colours or very friable medium, for example, where treatment should be avoided.

Exceptionally discoloured papers and papers with thick or absorbent structures often retain dissolved discolourations within themselves even after repeated soaking in immersion baths. If these papers are simply dried, the discolourations will remain in their structure. By placing such papers over a vacuum suction table, it is possible to evacuate the discolourants out of its structure. This procedure is quite effective on objects which have been floated over a water bath. In these cases, the diffusion of discolouration into water is not as effective as in immersion baths since the mobilized discoloration on the surface of the object often cannot penetrate downward to the water through the structure of the paper. The object is placed on a vacuum suction table face upward immediately after the removal from the flotation bath, and the discolouration is evacuated by the vacuum suction, with additional water applied from the surface by spray or brush application as the object allows. This procedure avoids tide marks and the mottling effect of discolouration which often are a problem in flotation cleansing.

Localized areas of discolouration on vulnerable objects with fugitive or friable media may be treated on a vacuum suction table. Discoloured areas are brushed with alkaline water mixed with an alcohol if necessary, and evacuated through the table, and additional fresh water is applied for final cleansing.

The vacuum tables presently in use are made with various methods and materials which reflect the needs and ingenuity of their individual makers and users. The table used by the author was designed by Robert Futernick of the Achenbach Foundation Conservation Laboratory using a vacuum-sealed aluminium Hexal panel and a wet-and-dry vacuum cleaner as the suction pump. I have used various other methods have been used based on the same working principles outside the studio; and in all instances it was helpful to use enough cushioning material between the object and the table surface so that the pressure from the vacuum suction would not distort the textures of paper and the medium. A sheet of blotting paper on top of a felt approximately ⅛" thick creates enough cushioning for my table.

Enzymal reduction of discolouration

Hardened and discoloured adhesives are very tenacious and difficult to remove by ordinary means from the porous, retentive structure of paper; so is the engrimed soil which is trapped among the interstices of paper fibres. Here, the mere cleansing action from water falls short of its function. High temperature often increases the cleansing effectiveness of water in these cases, and steam heat often helps remove the adhesives that react to high temperatures. But in these cases enzymes are generally a more effective cleansing agent than water.

The recent articles by Segal and Cooper[9] and by Hatton[10] describe their practical working procedures in the use of enzymes to release adhesives and to reduce adhesive stains and trapped soil in paper. More information is needed to establish the safety of enzymes in the treatment of paper, but the specificity of enzymes and the ease with which they can be denatured suggest a good safety potential for use not only as agents to facilitate the delicate and often time consuming procedure of removing the backing from an object, but also to reduce discolouration that is difficult to treat with other means.

The parameters of safety vary according to the nature of objects to be treated, and whether or not water and other agents may be used to eliminate residues and by-products of chemical substances utilized. The foregoing methods are by no means an exhaustive list of treatments possible for safe reduction of discolourations in paper, but are primary measures safe even for media that cannot withstand extensive cleansing. However, combining these means with skill and ingenuity can reduce discolourations considerably. And often in objects with fugitive or friable media, these are the only possible treatments we can apply to achieve any improvement in their visual effect.

As paper tends to retain substances or their harmful by-products to which it is exposed during the course of treatment, a large concern in using chemical bleaching agents is the elimination of harmful residues from the paper. If a bleaching method is available which does not employ a chemical bleaching agent, much of this concern may be eliminated. Bleaching with light is a method that does not employ chemical bleaching agents.

The experimental use of sunlight in bleaching of paper objects

The first chemical bleach, chlorine, was discovered by Karl Wilhelm Scheele in 1774. Before the use of

chlorine, sun bleaching was the only method of whitening the linen and cotton cloths that were used as fiber sources for papermaking. Cloth was soaked in extract of wood ashes and in sour milk, then was spread over a grassy meadow and exposed to sunlight with frequent sprinkling of water. Nascent oxygen emanating from the grass aided in the bleaching action[11, 12]. Sunlight has been used to bleach discolourations in the restorative treatment of paper objects for some time. Wächter[13] used sunlight effectively to bleach black and white graphics and Egyptian papyri, spraying the objects intermittently with water to keep them moist. Plenderleith[14] describes the method to reduce tea and coffee stains by exposing the affected areas to sunlight after applying an aqueous solution of potassium perborate. Annis and Reagan[15], in their recent study, describe the effect of sun bleaching on an old, undyed cotton fabric, exposing dry samples to the sun up to 32 hours, and report good results. The fabric samples noticeably brightened without a detrimental effect on fibre properties.

Over the past three years. I have experimented with the use of sunlight in bleaching discoloured paper. The method and observations are reported here. It goes without saying that all preliminary cleansing and washing must be carried out on paper previous to sun bleaching. Generally an immersion bath is used to irradiate paper with sunlight. Water mixed with magnesium bicarbonate solution *(c.* 0.2%) in the ratio of 5:1 is placed in a white photo-developing tray which is large enough to keep the shadow cast by the rim away from the paper. The paper should rest approximately 1'' or 2.5 cm below the surface of the water. For paper objects which cannot be placed in an immersion bath, a "moistening sandwich" is used. A blotting paper slightly larger than the dimension of the paper object is moistened with the mixture of water and magnesium bicarbonate solution and placed on a Plexiglas support. The paper object is also sprayed with the mixture and placed on the moistened blotting paper and a medium weight sheet of Mylar film is placed over its surface. The entire sandwich is then placed in the sunlight. The blotting paper supplies, and the Mylar film retains, the necessary alkalinity and moisture. Although frequent spraying is not necessary since the sandwich remains moist, sunlight warms the sandwich considerably if left alone during the course of irradiation, and occasional spraying on the surface of the paper object is necessary to keep it cool. Placing the sandwich on a screened rack or any other open support, will allow air to circulate and help reduce the temperature rise. The Mylar film also avoids the harmful effect of evaporating water to cellulose at a cellulose-air interface[16].

The exposure time in the sunlight varies according to the season and to the degree of discolouration of the paper but normally ranges between 2 to 4 hours. During this time the object should be turned to expose both sides.

As bleaching procedes, the solubilized discolourants are leached away into the bath or moistened blotting paper, but after the irradiation is completed the paper object is further cleansed by immersion in a clean water bath or, for objects which cannot be immersed in water, by application of moisture by spray or brush on a vacuum suction table to remove the solubilized substances remaining in paper. Deacidification procedure should follow the cleansing.

Hydrogen peroxide generated in water by sunlight is considered a major factor in sun bleaching. Since peroxide is known to cause damage to cellulose under acidic conditions[17], magnesium bicarbonate solution is added to the water to maintain an alkaline condition during irradiation. Additionally, the presence of the magnesium ion retards the degradation of cellulose in oxidative bleaching processes by deactivating the catalytic action of metal impurities such as iron and copper present in paper[18, 19], Richter[20] found that paper treated with magnesium hydroxide solution was well preserved after 100 hours of dry exposure to direct sunlight in Florida.

UF-3 Plexiglas, or a similar filtering material should be placed over the paper if the ultraviolet radiation in the sunlight is feared to cause an adverse effect. UF-3 filters all the ultraviolet radiation and a portion of the violet and blue range in the sun's spectrum. Even with this filtering, discolouration is reduced, although the bleaching action is slower and paper objects must be exposed to sunlight for a longer time (approximately 1 to 3 hours longer depending on the time of year and the degree of discolouration in paper) to achieve a satisfactory result.

With all bleaching methods, there is a risk of fading if colours are exposed to sunlight. However, it is possible to expose a local discoloured area to sunlight and block the penetration of light to undesirable areas by masking these areas with opaque paper or aluminium foil. If the colours present are not water-soluble, such as in Western colour prints, the 'moistening sandwich' unit can be used after masking areas where exposure is to be avoided. If any colours are water-soluble, the moistening should be limited to the stain and the adjacent areas. Care should be taken not to form tide marks in this case by leaching away the solubilized discolouration from the surface from time to time with dry

blotting paper and applying additional moisture by 'feathering' toward the adjacent areas. This method may give conservators a wider latitude in treating discolourations on objects with moisture-vulnerable media since the subsequent cleansing with water is far less compared with that required when a chemical bleaching agent is applied locally. The exposure time varies tremendously, but usually is shorter than that of overall bleaching so as not to cause unevenness of the paper tone.

Sun bleaching is not suitable for all papers. In fact sun bleaching should be used principally for rag papers made before the middle of the nineteenth century. Pure cellulose is a stable material and direct degradation of cellulose by sunlight is minimal[21, 22], and early papers were relatively free from light-sensitive impurities. But from about 1850, wood pulp was in prevalent use in papermaking. Lignin is an impurity in wood pulp and is know to be very unstable in light. It absorbs light, decomposes, and in doing so degrades paper. Papers with a high lignin content, such as groundwood papers, should not be subjected to sun bleaching as they can darken rather than brighten. The presence of lignin can be tested by a simple colour reaction of phloroglucinol solution applied to a fibre sample obtained from the paper in question[23]. About the same time as the use of wood pulp, alum rosin sizing came to be used in papermaking. Richter[24] reported that the presence of rosin endangered the stability of paper in dry exposure to the sun for 100 hours. Although it is not certain that alum rosin sized papers will be appreciably affected in the short irradiation time required in this method, it is a good policy to avoid sun bleaching them. Rosin size in paper can be detected by a characteristic ring when ether of a similar solvent is dropped in a spot on the surface of paper, or by observing the resistance of ink from feathering when applied to a crease[25].

Most papers industrially manufactured in the twentieth century contain mixtures of various fibres and chemical additives used as sizing, coating and filler, and it is impossible to detect what sunstances may exist in a given paper without a specialist's knowledge of paper analysis. Titanium dioxide, for example, is a pigment that came into use in the 1920s, and subsequently has come into wide use as a filler to increase the brightness and opacity of industrially made papers. This substance can cause photochemical degradation of cellulose. The detection of titanium dioxide filler requires more involved chemical tests than are feasible in a normal paper conservation laboratory. Since titanium dioxide and other photosensitive substances are found in modern papers, sun bleaching should be used cautiously with ultraviolet filtering. Further studies would be helpful to establish whether potentially harmful substances are in fact harmful during the short period of filterable irradiation required in sun bleaching.

Without forgetting the cautions and limitations mentioned above, some necessarily subjective observations on the remarkable results of bleaching accomplished by sunlight are presented below, but some scientific tests on sun bleached paper samples are now being peformed at the Cooperstown Graduate Program by Thomas Branchick under the supervision of Dr F. Christopher Tahk.

(1) The use of sunlight is a very effective bleaching method. Stains such as distinct matburns, dark foxing marks, wood stains and other pronounced discolourations that would require strong solutions of various chemical bleaching agents are satisfactorily reduced by single exposure. Since these tenacious discolourations are reduced simultaneously as the overall bleaching of the paper takes place it has not been found necessary to expose only the local discoloured areas. The only stains that do not reduce satisfactorily in sun bleaching appear to be those of metallic origin and dark pigmentation from mould growth.

(2) Paper treated by this method of sun bleaching regains considerable physical strength, increasing its body and elasticity. Degraded paper that was weak and brittle before treatment is more handleable and supple, regaining its 'rattle' in most instances. The recovered elasticity is observed in the ability of paper to flex more, and in the regained textural qualities of paper. The three-dimensional quality of relief and intaglio prints returns quite well. It is quite remarkable to see portions of paper which have been particularly weakened by wood stains and other highly degrading discolourations regain their normal strength and recover the appearance of the rest of paper. In chemical bleaching these areas most often persist in their weakness, and sometimes shatter in the presence of strongly alkaline bleaching agents or become spongy from the effervescence of certain bleaching agents such as sodium borohydride that disrupt the already weakened fibre bonding.

(3) The visual effect of sun-bleached paper is most pleasing. Paper has a warm white tone rather than the staring white brightness often observed in chemically bleached paper. The brilliant appearance of ink in black and white graphics is often remarkable. This probably is

due to the fact that the binding medium of the ink remains intact in the sun-bleaching method, whereas in chemical bleaching the medium may be affected by the strong alkalinity of the initial bleaching agent or by the antichlor subsequently used, or by both, which cause the ink to 'grey' slightly. It is also partly due, no doubt, to the congenial warm new tone of the paper interacting with the ink to create this lustrous effect. Additionally, the regained textural quality of the paper contributes to the subtle three-dimensionality of the image, enhancing its visual effect. The end result after necessary repair and gentle pressing is an object that appears natural without the forced whitened appearance of chemical bleaching. The restored object looks as it should and as it was meant to be.

No study has yet been made to the author's knowledge to assess the effect of sunlight on paper under the conditions discussed and evaluate its use as a bleaching agent for paper objects. Sunlight is a much-feared light source in conservation and its degrading effects to papers and textiles have been studied in detail[26]. However, these studies are normally carried out over long irradiation period (often 100 hours or more), and usually in dry exposure conditions. Full evaluation must await future studies of the soundness of this bleaching method which employs a short irradiation time and is carried out in the presence of water and magnesium bicarbonate. Until it can be proven safe, this method is simply presented as an alternative possibility to be considered in paper bleaching.

The use of sunlight as an irradiation source may pose a problem for many conservators who do not have an access to it year-around, and even where sunlight is present, air-pollution may pose a problem in urban areas. But xenon arc lamps and some fluorecent light sources produce a spectrum close to that of sunlight, and investigation of an artificial light source that would be practical for the use in a conservation laboratory is now underway in the project at the Cooperstown Graduate Program.

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2.2.2. The colour reversion of paper after bleaching

Helen D. Burgess

Investigations have been made on the colour reversion of both ligneous and rag fibre papers bleached as follows: pH 4.5 hypochlorite, pH 7.0 hypochlorite, pH 9.0 hypochlorite, chloramine-T, chlorine dioxide (immersion and gas methods), or stabilized hydrogen peroxide. The effect of antichlor (sodium thiosulphate or sodium borohydride) upon the rate of yellowing, as well as the possible influence of encapsulation of the paper artifact with 'Mylar' (polyethylene terephthalate) have been considered. The contribution of the extent of oxidation and chlorination of the cellulose and lignin components of the papers on the rapidity of colour reversion is discussed.

Introduction

All archivists and paper conservators have observed that some papers yellow as they grow older. They certainly have also noted that this yellowing behaviour is often related to poorer quality ligneous wood pulp papers and to poorly controlled storage environments. They deduce, quite correctly, that this yellowing is caused by degradation of the paper. The appearance of the yellow 'patina of time' is disturbing not only aesthetically but also since it is an indication of poor permanence. Any conservation treatment which will hasten this process is to be avoided. Since bleaching is probably the most degradative treatment to which an artifact might be subjected, it is particularly interesting to consider whether this process itself damages the paper sufficiently to increase the magnitude of the yellowing problem. The return of this brownish-yellow discolouration is referred to as colour reversion.

The problem of colour reversion has received much attention from the pulp and paper industry. The particular concern of the industry has been to identify what components of paper contribute to colour reversion, rather than to investigate which bleaching treatments minimize yellowing. In this study, however, both angles are considered. Before these results are presented, it is useful to briefly summarize the key findings published in the scientific literature.

It has been shown that colour reversion in wood pulps depends upon the species of wood, method of pulping, extent of digestion and type of bleaching treatment. Temperature, humidity and lighting conditions have also been implicated[1].

Oxidation of paper fibres promotes colour reversion due to formation of carbonyl (aldehyde and keto) and carboxylic acid functional groups[2,3]. Although earlier literature has ascribed this effect mainly due to the carbonyl groups[4], more recent studies indicate that the co-existence of the carboxyl groups is required[3].

The resin extractives (soluble in organic solvents) from wood pulp sources, when treated with an oxidative bleach during pulping, have been shown to be either a contributing factor or even an initiator in colour reversion[5,6].

The importance of chlorine residues in the reversion of wood pulp treated with chlorine-based bleaches (e.g. hypochlorites, chlorine dioxide or chlorite) has been established. The concentration as well as the presence of bound chlorine in the extrac-

tive component has a significant role[5, 7, 8] in the yellowing of paper. Bound chlorine is also found in the lignin portion of the paper fibres[9]. In the case of extensive pulping, the lignin portion of paper fibres is completely removed. However, if insufficient time or reagent is used, unstable chloro-quinones (intermediate reaction products of lignin with chlorine bleach) remain, especially if the subsequent washing is not adequate. These compounds are a key contributing factor in cololur reversion[9].

Colour reversion has also been linked to the susceptibility of a pulp to hydrolysis (i.e. whether a pulp may be quickly degraded by acid). This characteristic has been correlated to the presence of hemicelluloses[10]. These easily hydrolysable polymers yield fural and formaldehyde monomers on ageing which in turn polymerize to form coloured residues. The pH of a paper containing hemicelluloses would be very critical to its rate of colour reversion.

The need for natural ageing to supplement or replace accelerated ageing has been established by tests which show that 'yellowing involved in accelerated high-temperature testing did not correlate closely with that occurring during long-term storage in darkness'[6]. However, it has been shown that accelerated thermal ageing under certain conditions is closer to natural dark ageing than is accelerated photochemical ageing[11]. Good ageing results have also been obtained by sealing samples in glass tubes or storage envelopes to maintain normal moisture levels in the fibre[11, 12]. Recent guidelines[13] suggest that if it is necessary to use accelerated thermal ageing as a means of evaluating papers, the temperature be kept as low as possible (maximum 80°C). Certainly, the Tappi standard[14] for accelerated ageing (105°C) has very limited application for work of this type.

After reviewing the above literature, it became clear that it was important to compare the various bleaches used in conservation not only for relative rates of colour reversion, but also for (1) the level of chlorine residues and (2) whether a reducing agent treatment such as treating paper with sodium borohydride could reverse the long-term degradative effects of the oxidizing bleaches by decreasing the rate of colour reversion. Sodium thiosulphate, being a much weaker reducing agent, could not be expected to be as effective. Only reversion in the dark is considered here (exposure to light would undoubtedly accelerate the reversion process but is beyond the scope of this project).

Some wood pulp papers which were used in an early part of this study were encapsulated in Mylar (polyethylene terephthalate) (see below). A very rapid rate of reversion was noted for these samples. It was therefore decided to investigate whether encapsulation affects the rate of colour reversion.

Examination of the results pertaining to chloramine-T bleaching showed that a phenomenon in addition to colour reversion was taking place during storage. This bleach is not discussed and compared with the other bleaches on pages 61—67, but will be treated as a separate entity in the final section of this paper.

Experimental methods

Electronbeam microanalysis of chlorine in paper.

Sheets of paper from two books, (1) laid rag (linen fibre) paper (published in London in 1794) and (2) machine-made ligneous (wood pulp fibre) paper (published in Paris in 1889), were bleached for 10.0 min each using one of the methods outlined below. For both paper types, the sheets to be used were taken from a single section.

After washing and drying, the papers were analysed using electronbeam-microanalysis. Carbon-coated paper samples were prepared as for standard scanning electron microscopic examination. At 50× magnification one square millimetre areas of paper surface were scanned and analysed for chlorine content. Each of two samples from a duplicate set was analysed 16 times, with 4 replicate determinations on 4 areas, so that each bleaching method was analysed a total of 32 times for each of the two papers. A calibration experiment using paper impregnated with sodium chloride was set up to ascertain that the findings from microanalysis do vary linearily with the true chlorine content (i.e. that the instrumental method[15]employed was quantative).

The experimental papers

Five different papers were used in the colour reversion experiments described:

(1) A linen rag paper (results on page 61) from a cloth-bound scrap book dated, prior to 1874 (place of manufacture unknown).

(2) A mechanical wood pulp paper (results on pages 62-63) from a book entitled *Modern Explorers,* published in the USA and dated 1909.

(3) A mixed fibre (wood pulp and linen) paper (results on pages 63-65) from a book entitled *Practical Helps For Every Home,* published in the USA in 1893.

(4) A linen rag paper (results on pages 65-67) from a cloth-bound banker's ledger in which the earliest record was dated 1899.

(5) A mechanical-wood pulp paper (results on pages 65-67) from a paper-bound scrapbook manufactured in the USA *circa* 1932.

Preparation of bleach solutions

The bleach solutions used in this study were sodium hypochlorite (buffered to pH 4.5, 7.0 or 9.0), chloramine-T, chlorine dioxide (immersion and gaseous methods) and stabilized hydrogen peroxide. The procedures were carried out at room temperature (20°C) with less than 2°C variation among the various treatments. Deionized or distilled water was used in preparation of all the solutions.

Each litre of the three sodium hypochlorite (NaOCl) bleach baths (concentration of either 1 or 2% available chlorine) was prepared by the addition of 400 ml of the appropriate 1 M buffer (pH 4.5 sodium acetate, pH 7.0 sodium phosphate, or pH 9.0 sodium borate) to the appropriate amount of a stock solution of NaOCl (laboratory grade, 4-6% available chlorine). The individual baths were adjusted to a pH of 4.5, 7.0 or 9.0 by the addition of acetic acid (pH 4.5 bath), phosphoric acid (pH 7.0 bath) or boric acid (pH 9.0 bath). The solution was made up to the correct volume with water and the pH checked once again.

Each litre of chlorine dioxide bleach (for either immersion or gas treatments) was generated at room temperature by the addition of 20 to 25 ml of formaldehyde to 980 ml of an aqueous solution containing 20 g sodium chlorite (reagent grade).

Each litre of stabilized hydrogen peroxide (H_2O_2) bleach (concentration of either 1 or 2% H_2O_2) was prepared by adding magnesium sulphate (5 g), sodium silicate (7.5 ml of 41° Be (4.9 M) solution) and hydrogen peroxide (30% w/w H_2O_2, reagent grade: 33 and 67 ml respectively for the 1 and 2% solutions) to either 960 ml (for 1% bath) or 925 ml (for 2% bath) of an aqueous solution containing sodium hydroxide (5 g) and sodium carbonate (5 g). The pH was checked and adjusted to 10.0 with acetic acid when necessary.

Bleaching of papers

Experimental samples were prepared from each of the five papers described above. For each treatment sequence[16] studied, four samples of each type of paper were used, and the reflectance at 416 nm was determined as an indicator of the degree of yellowing. The analysis was carried out using a Beckman Acta MVI Spectrophotometer fitted with an integrated sphere reflectance attachment using barium sulphate as reference standard. The 416 nm wavlength[17] was chosen to avoid interference from the light blue lines (writing spaces) which were present on Paper 4. The usual wavelength for detection of yellowing of paper is 457 nm.

The procedure for the bleaching experiments was as follows:

Paper 1: The papers were prepared for bleaching by soaking in deionized water for about 5 min. Samples were bleached for five different periods of time (usually 1, 2, 4, 6 or 8 min) for each method chosen, by immersing them in a tray containing 1 litre of bleach. The concentrations of the hypochlorite and peroxide bleaches were 1%, chlorine dioxide (immersion) 2%, and the chloramine-T bath was 4%. After removal from the bath, the bleaching action was terminated by rapid immersion in 3.0 litre of 2% sodium thiosulphate. After 15 min the samples were transferred to a washing tray and washed in running tap water for about 1 h to remove residual chemicals. The samples were dried between acid-free blotters and after approximately 18 h, the reflectance was measured.

Paper 2: The samples were treated as described for Paper 1 but with the following changes: The bleach concentrations were 2% for all methods except for chloramine-T which used a 4% bath. The bleaching times were usually 2, 5, 8, 11 or 15 min. The chloramine-T bleached samples were anti-chlored with either sodium thiosulphate or sodium borohydride. The sodium borohydride was also used at a 2% concentration and in a manner similar to the thiosulphate. Enough samples were prepared to allow for both encapsulated and unencapsulated natural ageing of papers.

Paper 3: The samples were treated as described for Paper 1 but with the following changes. The bleaching of the paper was carried out in chemically inert photographic tanks (20 × 10.8 × 16.3 cm) containing 3.0 litre of bleach. The papers were immersed vertically by suspending them on 10 × 12.5 cm stainless steel photographic hangers[18]. The bleaching times were as for Paper 2 except for the pH 4.5 hypochlorite, where 3, 6, 11 16 or 22 min were used.

Paper 4: The samples were teated as described for Paper 2 but with the following changes. Gaseous chlorine dioxide bleaching (as well as the immersion) was performed with samples from both Papers 4 and 5 bleaching concurrently to ensure identical reaction conditions.

Gas bleaching was carried out using a large (10.5 × 67.5 × 7.5 cm) tray containing 6.0 litre of formaldehyde-activated sodium chlorite. The samples were dampened (slightly) on both sides with distilled water and then placed on a large screen (95 × 70 and 25 cm suspended from bottom) with the side to be analysed facing up. The samples included papers which were to receive no after-treatment at all as well as those to be treated with

either thiosulphate or borohydride anti-chlors (plus washing). The screen was lowered into the tray and suspended 1.5 cm above the surface of the solution. A clear Plexiglas cover was put into place (a vent allowed for gas escape in order to prevent possible explosion) to contain the gas. The samples were bleached for 15 min.

The samples for the other six methods of bleaching were also anti-chlored with either sodium thiosulphate or sodium borohydride followed by washing, but no samples were left untreated after bleaching. A single bleaching time of 10 min was used for these experiments. Samples were aged by both natural (encapsulated and unencapsulated) and accelerated thermal ageing methods.

Paper 5: The samples were treated as described for Paper 4 except that no papers were prepared for accelerated ageing.

Ageing of paper

The samples were aged in one of three ways:

(1) Natural ageing in the dark. The samples were interleaved with neutral pH tissue and kept in a drawer (T°C—22°C and RH from 30 to 60%).

(2) Natural ageing of encapsulated samples. Samples (number varied from 1 to 10 depending on size) were encapsulated using a rectangular Mylar (.005 in, Type D) envelope held together by strips of 3 M 415 Double-Sided Tape. Breather spaces of about ⅛ in were used at each corner. The envelopes were placed in drawers for the ageing period.

(3) Accelerated Ageing. The papers to be aged were interleaved with sheets of Mylar and slipped into Kodak Cold Storage Envelopes of appropriate size and heat sealed. The envelopes were placed in a circulating air oven with no RH control at 75°C and left for 28 days.

The individual papers were aged as follows and then analysed for the extent of yellowing by measuring the reflectance at 416 nm:

Paper 1: Natural ageing in the dark (Method 1) for 12 months.

Paper 2: Natural ageing in the dark (Method 1) and encapsulation (Method 2) for 5 months.

Paper 3: Natural ageing in the dark (Method 1) for one month and then the same papers encapsulated (Method 2). Monitoring of the reflectance was performed at both 4 and 12 months after bleaching.

Paper 4: Natural ageing in the dark (Method 1) and encapsulation (Method 2) for 74 days, as well as accelerated ageing (Method 3).

Paper 5: Natural ageing in the dark (Method 2) for 74 days.

Results and discussion

Analysis of water-insoluble chlorine residues

The quantities of residual chlorine in the various papers (as determined by electron microanalysis) may be compared by giving the concentration levels as ratios of one another. Since hydrogen peroxide does not involve any chlorine containing compounds, its chlorine level may be assumed to be background. Therefore, the value for the chlorine level in the hydrogen peroxide bleached papers may be set at unity with the data for the other methods reported as numbers relative to this base standard. The data for rag paper is shown in *Table 1* and ligneous wood pulp in *Table 2.17*. Data is presented only for those papers which contained statistically significant chlorine levels.

Table 2.17 Analysis of bleached rag paper for residual chlorine

Bleaching method	*Relative chlorine level*
Stabilized hydrogen peroxide	1.0
Immersion chlorine dioxide	1.1
Chloramine-T	1.1
pH 7.0 hypochlorite	1.7
pH 4.5 hypochlorite	1.8

Table 2.18 Analysis of ligneous wood pulp paper for residual chlorine

Bleaching method	*Relative chlorine level*
Stabilized hydrogen peroxide	1.0
Chloramine-T/borohydride anti-chlor	2.1
Chloramine-T/thiosulphate anti-chlor	3.1
Immersion chlorine dioxide	6.5
pH 9.0 hypochlorite	8.5
pH 7.0 hypochlorite	20.2
pH 4.5 hypochlorite	29.5

The error of the technique is such that confidence in real differences in chlorine content can be assumed only when this difference is close to or greater than one (based on the values presented in *Tables 2.17 and 2.18).* In *Table 2.17*, it may be seen that only the pH 7.0 and 4.5 hypochlorite methods give statistically significant chlorine levels. It is not possible to say which of these two methods introduces more chlorine into the paper.

The data for ligneous paper samples presented in *Table 2.18* show much higher chlorine levels. All bleaching methods exhibit significant chlorine residues. This clearly shows the preferential formation of chlorine complexes with lignin over cellulose. Furthermore the bleaching methods can be differentiated on the basis of the relative quantities of chlorine residues remaining after bleaching. There are several explanations but the most likely is that the differences arise from variation in the rate of the chlorination reactions.

As shown in *Table 2.18* the hypochlorite bleaches give the highest chlorine levels with acidic conditions favouring the formation of stable chlorine complexes. The mechanisms of chlorination during acidic hypochlorite bleaching are probably different from those in operation during aqueous chlorine dioxide bleaching (pH of bleach bath about 5.5). An indication of this is the large difference in chlorine residues obtained.

The amount of chlorine remaining in ligneous paper bleached with chloramine-T varies slightly, depending upon whether the samples were antichlored with sodium borohydride or sodium thiosulphate. Although this difference is at the lower end of our ability to differentiate chlorine levels, it is apparent that the borohydride treated samples do contain less chlorine, probably because the borohydride is a more effective reducing agent than is the sodium thiosulphate.

Bast fibre paper

The colour reversion of bleached paper composed of linen rag fibres is shown as a plot of reversion (ΔA_{416}) vs time of bleaching (*Figure 2.25(a)*). (Chloramine-T bleaching is discussed below). The ranking of the bleaches, in terms of the relative degree of colour reversion, corresponds to the rate at which they oxidize cellulose[19] (main component of linen rag fibres):

(1) Stabilized hydrogen peroxide
(2) Immersion chlorine dioxide
(3) pH 9.0 hypochlorite
(4) pH 4.5 hypochlorite
(5) pH 7.0 hypochlorite

For none of the bleaches, except the extremely degradative pH 7.0 hypochlorite, did the extent of reversion (value of ΔA_{416}) depend greatly on the bleaching time (i.e. slope of curve is almost zero). The reactions which promote colour reversion appear to occur early in the bleaching process. The concentration of carbonyl and carboxylic acid groups has been shown to increase with bleaching time[19] but apparently not rapidly enough to influence the rate of yellowing of rag paper (again, except for pH 7.0 hypochlorite bleaching).

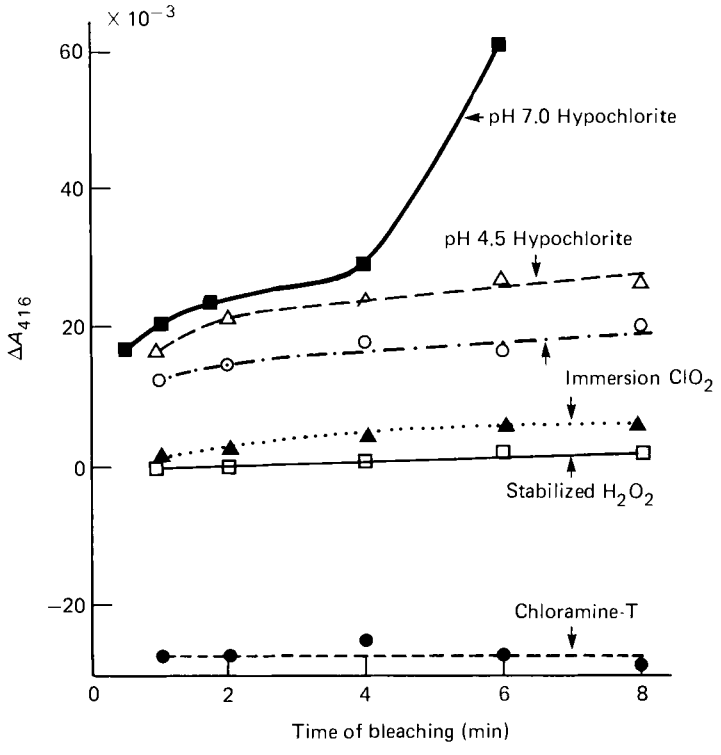

Figure 2.25(a). Colour reversion of bleached rag paper after natural ageing for 12 months in the dark.

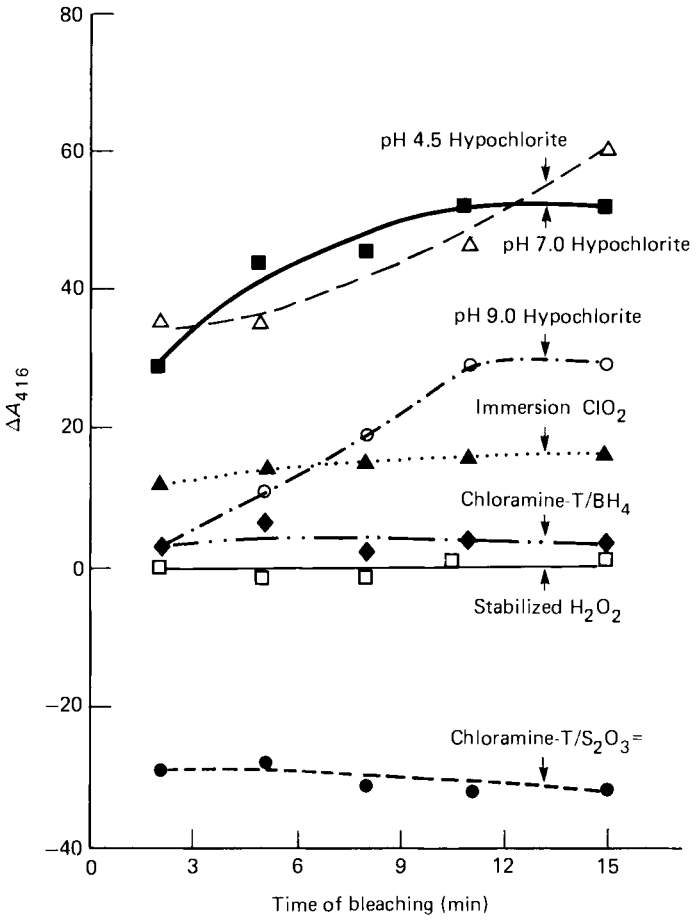

Figure 2.25(b). Colour reversion of bleached ligneous paper (encapsulated) after natural ageing for 5 months in the dark.

Wood pulp paper

Colour reversion in ligneous wood pulp paper is much more complicated (see *Figures 2.25(b)* and *2.26*). The most startling difference in this paper, as compared with the bast fibre samples, is the very rapid reversion. In 5 months the extent of yellowing of the lignin papers had exceeded that of the bast fibre papers which had been aged for 12 months. Some of the papers had reverted to a brightness level similar to that observed before bleaching.

For cellulosic rag paper *(Figure 2.25(a))*, the ranking of the six bleaching methods, in terms of colour reversion, was the same for all bleaching times. However, this behaviour was not observed for bleaching of ligneous fibres with chlorine-containing species. It is evident that more than one chemical process took place. The rate of each was dependent not only upon the particular bleach used, but also on the reaction time (i.e. bleaching time).

A partial explanation may be given by the observation that reversion appears to correlate with levels of water-insoluble chlorine residues (see above) detected in bleached papers as well as their lignin content. A rapid reversion of lignin fibre papers corresponds to high chlorine levels, while the slower reverting bast fibre papers exhibit much lower or non-existent quantities of bound chlorine. For the lignin paper, the relative order of bleaches, in terms of reversion, corresponds more closely with their chlorine levels than with the relative rates of oxidationof cellulose (as discussed above).

In the presence of a chlorine-containing bleach, a key reaction of wood pulp paper is chlorination of the lignin. Rag paper fibres, containing mainly cellulose, also form chlorine intermediates but they are much less stable than the lignin-chlorine complexes[20]. The lignin in the wood pulp paper is amorphous and so is completely available for reaction with the bleach. Reaction will therefore tend to progress during the initial stages of bleaching, causing the concentration of chlorine complexes (which in turn promote colour reversion) to steadily increase. Cellulose, however, is largely crystalline and so does not provide as many sites for reaction. It is also important to remember that other natural components of wood such as hemicelluloses and resin extractives are present in those wood pulp papers manufactured from pulps

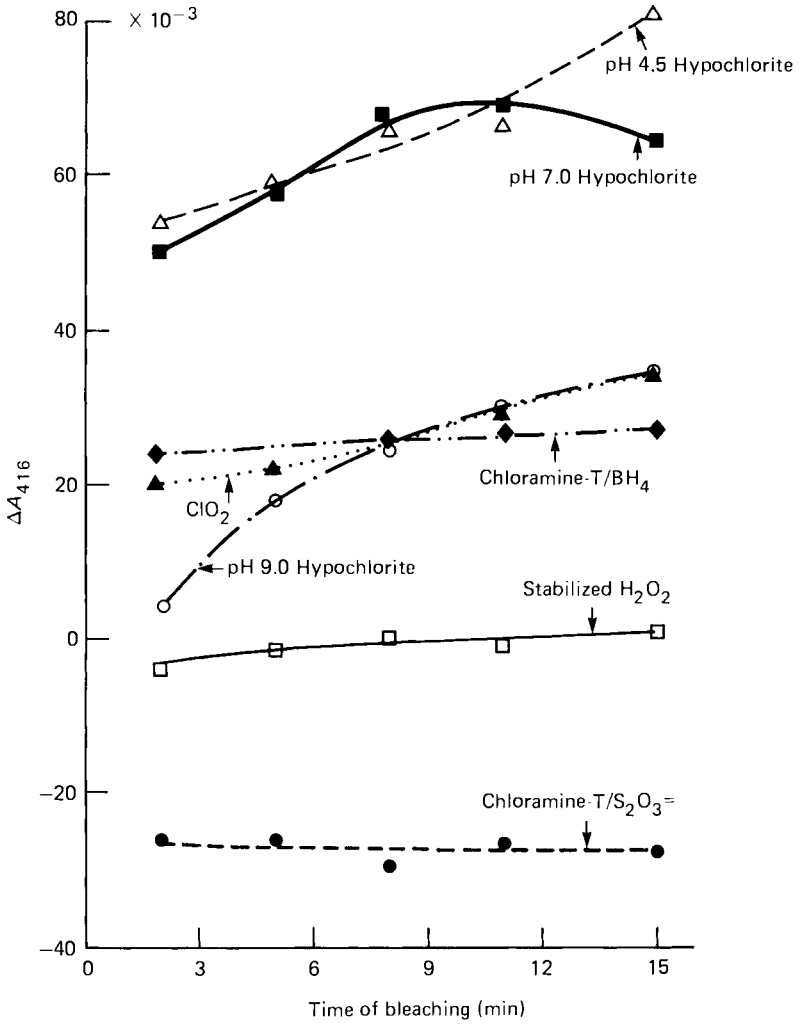

Figure 2.26. Colour reversion of bleached ligneous paper (unencapsulated) after natural ageing for 5 months in the dark.

which received only minimal pulping (i.e. no chemical treatment). The presence of these components has been shown to be critical in the colour reversion of paper and so must be considered. It is also clear that acidity must play some part, although its significance, in relation to the chemical considerations discussed above, is uncertain.

Encapsulation of wood pulp samples after bleaching resulted in a reduced rate of colour reversion. In some cases, such as when pH 4.5 hypochlorite, pH 7.0 hypochlorite or chloramine-T was used with sodium borohydride as anti-chlor, the differences were very large (change of about 20 units). For the pH 9.0 hypochlorite and immersion chlorine dioxide the differences were smaller (change of less than 10 units) and for chloramine-T (with sodium thiosulphate anti-chlor), and stabilized hydrogen peroxide, there were only very small changes. However, the relative position of the curves in *Figures 2.25* and *2.26* were similar for encapsulated and non-encapsulated papers except for the immersion chlorine dioxide and chloramine-T (sodium borohydride anti-chlor) methods.

It is unclear why encapsulation slows down reversion. The breather spaces at all corners and the porosity of the Mylar film eliminates the possibility of oxygen starvation causing a reduction in the oxidation reaction. However, by placing humidity cards in the envelopes, it was observed that the effect of the encapsulation was to slow down changes of relative humidity which took place in the surroundings, from minutes to several days. This 'buffering' of humidity changes reduces stress and hence could perhaps reduce colour reversion.

Mixed fibre paper

The results for the colour reversion of a paper composed of linen and ligneous wood pulp fibres are shown in *Figures 2.27* and *2.28*. This paper[21] had characteristics somewhere between those discussed above. One difference in behaviour for this paper is that the pH 4.5 hypochlorite bleached samples revert more rapidly than the papers bleached with hypochlorite at pH 7. The mixed

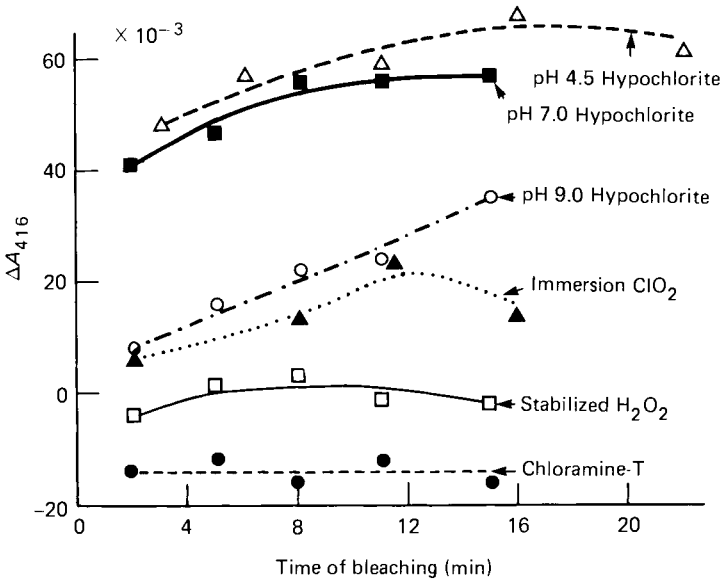

Figure 2.27. Colour reversion of bleached mixed fibre (wood pulp and linen) paper after natural ageing for 4 months in the dark.

fibre paper differs from the bast fibre paper *(Figure 2.24)* in that the rate of chlorination of lignin (and any other component of the wood pulp fibres which may react) becomes more important than the rate of oxidation of cellulose for hypochlorite bleaches.

All of the reversion curves for the bleaching of the mixed fibre paper show a well-defined separation (i.e. the curves may be distinguished easily from one another at all bleaching times). The mixed fibre paper does not exhibit the large difference in reversion between the pH9.0 hypochlorite and immersion chlorine dioxide bleached samples as was observed for rag papers (see above). The behaviour of this mixed fibre paper is similar to that observed for pure wood pulp samples. Comparison of *Figures 2.27* and *2.28* demonstrates that the yellowing progresses steadily, although its rate diminishes over time so that much more reversion took place during the first four months than in the subsequent eight months. As before, chloramine-T is exceptional and will be considered later in this discussion. In *Figure 2.29* are compared examples (the degradative pH 4.5 and 7.0 hypochlorite bleaching methods) of reversion at 4 and 12 months, which show that reversion continues unabated over long periods.

The rate of yellowing (reversion) for the mixed fibre paper is fairly close to that of the wood pulp paper; considerably faster than the rate for rag papers. The quantity of better quality fibres in this paper does not appear to affect the reversion rate. The harmful characteristics of wood pulp dominate.

Alkaline hypochlorite bleaching of wood pulp

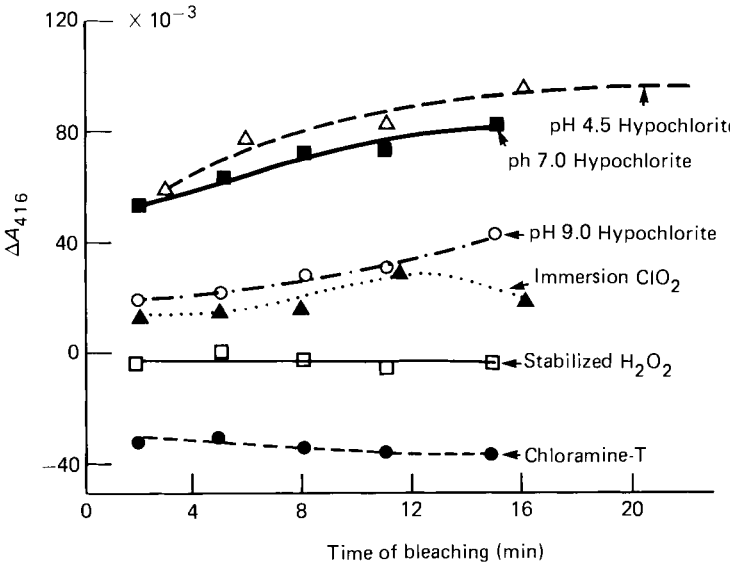

Figure 2.28. Colour reversion of bleached mixed fibre (wood pulp and linen) paper after natural ageing for 12 months in the dark.

has been shown to favour the formation of carboxylic acid groups over carbonyl groups[22] the reverse being true for acidic hypochlorite bleaching. Therefore if carbonyl groups are a more important factor in reversion than are carboxylic acids, the *pH 9.0* curve in *Figures 2.28* and *2.29* should show less reversion than the *pH 4.5*[23]. The immersion chlorine dioxide and hydrogen peroxide oxidation of wood pulp have been reported[24, 25] to result mainly in formulation of carboxylic acid groups and so are expected to show less reversion than the carbonyl-producing acid hypochlorite. This was observed for the bleaching of the mixed and bast fibre papers, which lends support to the theory that the formation of carbonyl groups is important to colour reversion. The lignin papers do not present as clear a result as do the bast and mixed fibre papers, but this may be ascribed to the higher level of chlorination of the poorer quality paper.

chlored or washed reverted less than either the immersion chlorine dioxide (thiosulphate anti-chlor) or chlorine dioxide gas (thiosulphate anti-chlor) treatments. A control experiment[27] (No. 9) did show substantial colour reversion of samples which were only treated with anti-chlor (either thiosulphate or borohydride) and then washed. The rate of yellowing of rag papers appears to be diminished by treatment with sodium borohydride. The borohydride reverses the degradative effects of oxidative bleaching: presumably, the carbonyl groups are reduced to harmless hydroxyl groups. The success of this reversal for all of the bleaches is evident in the greater overall similarity of rates of reversion (as compared with the big difference with the thiosulphate anti-chlor). Since sodium thiosulphate is a much weaker reducing agent than sodium-borohydride, it is only able to eliminate residues of active bleach and is not capable of reducing the oxidation products.

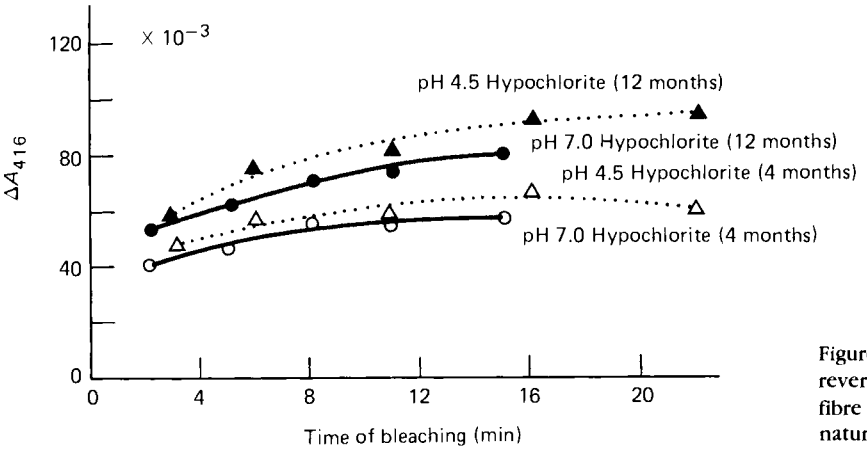

Figure 2.29. Comparison of the colour reversion of hypochlorite bleached mixed fibre (wood pulp and linen) paper after natural ageing for 12 months in the dark.

Sodium borohydride treatment of paper

The histograms shown in *Figures 2.30* and *2.31* illustrate the colour reversion behaviour of rag and ligneaous wood pulp papers which had been bleached and anti-chlored with either sodium thiosulphate or sodium borohydride. The selection of 10.0 minutes for the bleaching time represents a reasonable upper limit[26] for the length of time which an artifact can safely remain in a bleach bath.

For linen rag paper bleached with hypochlorite *Figure 2.30,* No. 1-3) the samples treated with sodium thiosulphate show the same relative order in extent of reversion as do the bast fibre samples *(Figure 2.24)* although the latter have been subjected to natural, not accelerated ageing. The chlorine dioxide and peroxide bleached papers (Nos 4-7) all revert at about the same rate: The samples treated with ClO_2 gas which were not anti-

The accelerated ageing experiment with bast fibre papers discussed in this section is only a preliminary investigation of the effect of borohydride anti-chlor on bleached bast rag papers. A similar set of samples is presently being aged naturally (in the dark). Early indications are that results closely follow those of the thermally aged samples.

The effect of the anti-chlor used as well as the influence of Mylar encapsulation was studied for the ligneous wood pulp paper *(Figure 2.31).* Sodium borohydride does not have the same beneficial effect on lignin-containing paper as it does on the bast fibre. In most cases (except for pH 4.5 and 7.0 hypochlorite) sodium borohydride actually increases the degree of reversion (relative to the brightness after bleaching and anti-chlor treatment).

This interesting trend can be understood by considering the chemistry of the conservation sequences involved as well as the materials being

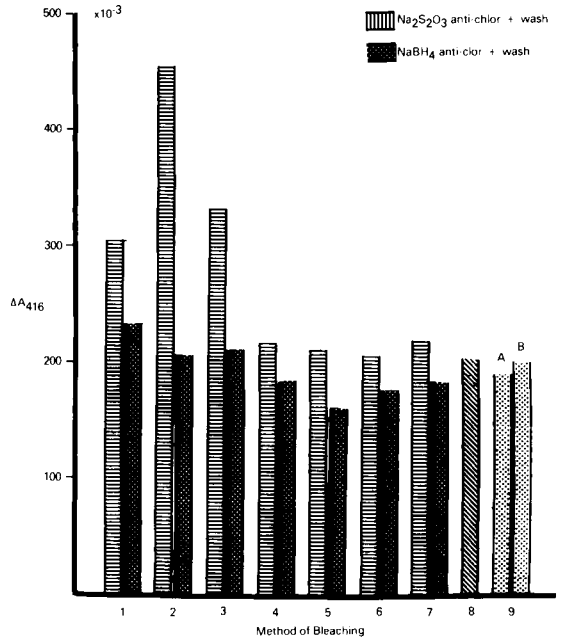

Figure 2.30. Colour reversion of bleached rap paper after accelerated thermal (75°C for 28 days)

treated. The lignin paper before treatment is very yellow (average reflectance at A_{416} about 0.6) while the linen samples are only mildly so ($A_{416} \triangleq 0.25$). Even the most powerful bleach (i.e. pH 7.0 hypochlorite) is not capable of brightening the lignin paper as much as the strongly reducing sodium borohydride. The borohydride is, itself, an effective bleach[28, 34]. The brightest paper is of course, achieved by the combination of a strong oxidizing bleach followed by the borohydride reducing agent. Since the rag paper is much less yellow, there is a smaller possible change in brightness upon bleaching. For both types of paper a certain proportion of the brightness obtained by use of a reducing agent will be easily reversible by atmospheric oxygen over relatively short periods. Therefore, the lignin paper which was greatly brightened by the conservation treatment (bleach + borohydride anti-chlor) will be more likely to show a larger absolute change in colour (i.e yellowing) with ageing than will the rag paper which had not been brightened as much initially.

When considering the reversion results of the (unencapsulated) lignin papers in more detail, the ranking of the bleaches in terms of their brightness stability is not very different from the results of the other ligneous papers. In bleaching with hypochlorites, the pH 4.5 bleach has the fastest rate of reversion, followed by the pH 7.0 and pH 4.5 bleaches. The chlorine dioxide methods (not considering the borohydride treated samples) revert at about the same rate as does the pH 9.0 hypochlorite. The peroxide undergoes the least change in brightness during ageing.

The hypochlorite bleached samples treated with sodium borohydride had a similar ranking to that discussed above with papers bleached with stabilized hydrogen peroxide yellowing the least. However, the unencapsulated chlorine dioxide samples (borohydride anti-chlor) revert far more rapidly than the pH 9.0 hypochlorite samples

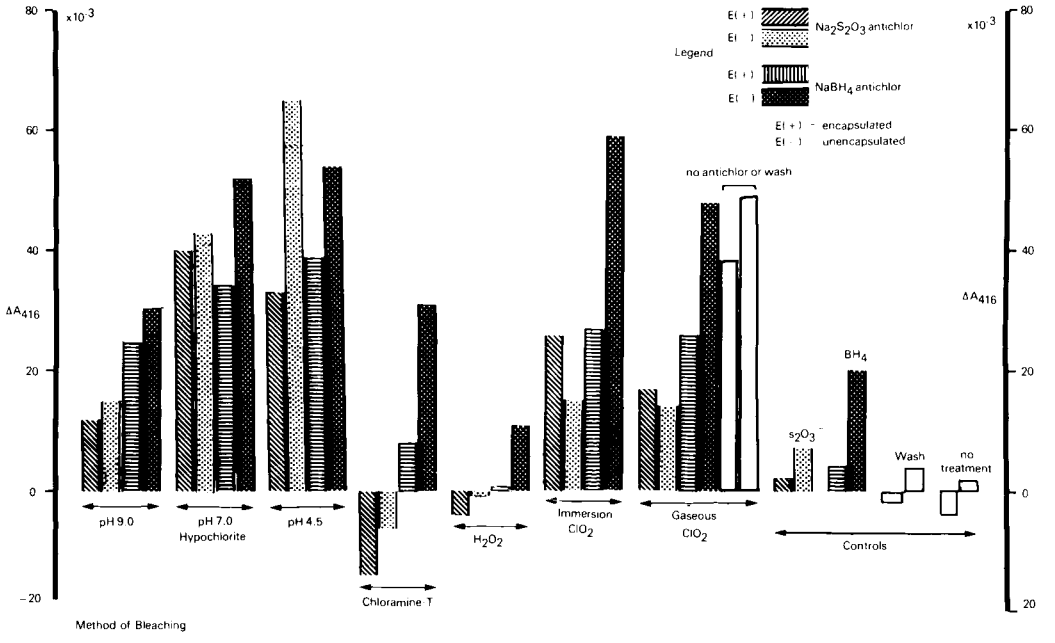

Figure 2.31. Colour reversion of bleached ligneous papers after 74 days in the dark.

(contrary to results reported above); this reversion is diminished by encapsulation.

The chlorine dioxide bleaching of the lignin papers has some very interesting results. Unlike the bast samples *(Figure 2.30)* the gas bleached samples which were not washed revert far more rapidly than do other chlorine dioxide treatments (except for unencapsulated borohydride samples, which probably have a faster rate of reversion for the reasons discussed above). The necessity of washing and thus solubilizing the heavily chlorinated bleaching products is much more important for wood pulp than it is for rag fibres. The extent of reaction of the bleach with the paper is probably much less for the cellulosic rag fibres that it is for the ligneous wood pulp; therefore the unwashed bleached rag papers revert far less (relative to the other bleaching methods) than do the wood pulp papers.

In general, it can be said that encapsulation of the lignin papers retards colour reversion; the only exceptions are the chlorine dioxide bleached samples (both immersion and gas) which have been anti-chlored with thiosulphate. It is unclear why these samples differ in this regard, especially when the unwashed chlorine dioxide gas samples also revert less when encapsulated. However, the overall trend, particularly for those samples which have very fast rates of reversion when unencapsulted, is that encapsulation retards colour reversion. It must be acknowledged that a study based on only one bleaching time (in this case 10.0 min) cannot be as clearly interpreted as one which follows reversion at several times over an extended period of bleaching. However, the reliability of this approach is supported by the observations above for bast and mixed fibre papers which showed identical ranking of the relative rates of colour reversion over all the bleaching times studies.

Chloramine-T bleaching

Substantial brightening of chloramine-T bleached papers can occur during dark storage. It has been suggested in the literature[29] that chloramine-T is not easily removed from papers by water washing, especially if alum is present in the paper, but it has also been assumed that the use of an anti-chlor such as sodium thiosulphate will eliminate the bleach residues and hence any problems associated with them. The results presented in the foregoing discussion prove that this is not true. Residues do remain and are capable of effecting large changes not only visually (i.e. brightening) but probably chemically as well. It is probable that this change is caused by an oxidative degradative process which weakens the paper fibres as it proceeds. Inevitably, no control can be exercised over the final degree of brightness if this method is used.

Examination of *Figures 2.27* and 2.88 reveals that the brightening of papers bleached with chloramine-T progresses over a long period with only a slightly diminishing rate: almost as much brightening occurred during the first four months as during the following eight. It is a little surprising that an oxidizing agent is stable enough to continue bleaching over an extended period, although this can probably be attributed to the physical and chemical effects of complex formation between the bleach residues and the fibre.

Use of sodium borohydride (a stronger reducing agent than thiosulphate) can eliminate this brightening effect *(Figures 2.25* and *2.31)*. In fact, substantial colour reversion of these samples occurs. This lends support to the suggestion that an oxidizing agent[30] is responsible for the brightening effect, because sodium borohydride is capable of eliminating a wide variety of oxidizing agents.

The experimental observations for linen fibre provide an interesting exception to this progressive whitening phenomenon *(Figure 2.30)*. These results are not caused by the accelerated ageing since naturally aged samples also yellow rather than brighten. This linen paper is different from the others in one important respect; it does not contain as large a quantity of inorganic impurities. In fact X-ray diffractometry[31] indicates that the rag paper is fairly similar to Whatman No. 1 filter paper (a low ash cellulosic paper) in this respect and that the other papers studied have many more impurities. It is probable that many inorganic impurities could aid in complexing chloramine-T (and prevent its dissolution and removal by washing) in a manner similar to the mechanism suggested for alum[29].

Since it has been suggested that the alum ($Al_2(SO_4)_3$) in paper may prevent chloramine-T from being fully removed (by washing) after bleaching[29], attempts were made to estimate the aluminium levels in the papers studied[32]. The preliminary investigations show a very wide range of concentrations for each individual paper type; perhaps due to variations across the paper sheet itself. The data for the aluminium content for these papers (expressed in the arbitrary units as relative concentration levels) are in *Table 2.19*.

The linen paper (Paper 4) which did not 'whiten' during the ageing *(Figure 2.30)* has the lowest concentration of alum (fairly close to the Whatman No. 1 standard) while the other experimental papers are much higher. This correlates well with the suggestion that this paper does not contain bleach residues (since there are few impurities to complex them) and so reverts during ageing.

Table 2.19 The aluminium content of experimental papers

Paper type (see page 60 for description of each paper)	Aluminium content
1	630
2	510
3	420
4	170
5	480
Whatman No. filter	0

Conclusions

(1) The colour reversion of rag papers may be ranked in the following order of decreasing brightness stability:
   (a) stabilized hydrogen peroxide
   (b) chlorine dioxide (immersion and gas methods)
   (c) pH 9.0 hypochlorite
   (d) pH 4.5 hypochlorite
   (e) pH 7.0 hypochlorite

When lignin and resin extractives (e.g. from wood of jute pulps) are present in the paper fibres the rate of reversion for the chlorine dioxide methods tends to approach that of the pH 9.0 hypochlorite procedure. The pH 4.5 hypochlorite method of bleaching results in papers which revert at a rate at least as rapid, and usually faster than, samples treated by pH 7.0 hypochlorite.

(2) Sodium borohydride treatment of rag paper substantially decreases the rate of colour reversion for all bleaching treatments. The use of reducing agents such as the borohydride shows promise as a means of controlling the yellowing of bleached papers during storage. However, since the correct reaction conditions and methods of handling have not been defined, the method cannot be recommended for general use yet[33].

(3) Ligneous wood pulp papers show a faster rate of reversion when treated with sodium borohydride than with sodium thiosulphate. However, the vastly increased brightness obtained with the borohydride ensures that these papers maintain a real brightness level (at least within the period of this experiment) which is superior to the thiosulphate anti-chlored samples.

(4) Many paper types which have been bleached with chloramine-T will continue to brighten substantially during storage. This suggests that bleach residues remain, which sodium thiosulphate is incapable of removing (within the time period and reagent concentration used for the anti-chlor treatment). Sodium borohydride treatment does completely remove the bleaching residues[55]. The result of this borohydride treatment would be a paper which reverts at a rate similar to a sample bleached with dilute pH 9.0 hypochlorite and then anti-chlored with sodium borohydride. However, sodium borohydride at the concetrations used herein causes paper to be bleached far in excess of a simple chloramine-T treatment. Careful regulation of the con centration of anti-chlor to control this brightening effect is required.

(5) Mylar encapsulation of both rag and wood fibre papers slows down the rate of colour reversion. There is some evidence that humidity changes within the paper (which may be a contributing factor in the rate of subsequent colour reversion), are probably buffered by encapsulation.

Notes and References

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17. The justification for use of this wavelength will be published in a forthcoming paper entitled: 'A comparative study of the bleaching efficiency of six bleaching systems'.
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26 This depends upon many variables such as the nature and condition of the artifact under treatment, the bleach being used (as well as its concentration) and bath temperature.
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31. The X-ray diffractometry was performed by James Argo of the Analytical Research Services section at the Canadian Conservation Institute (CCI). Ottawa, Canada.
32. The aluminium concentrations were estimated using atomic absorbtion techniques by Marilyn Laver of the Analytical Research Services at the CCI.
33. The main problem is the copious liberation of hydrogen gas during treatment. It is possible that this 'bubbling action' could damage artifacts in poor condition. Investigations are

presently under way to study ways of countering this problem. Possible difficulty with reductive bleaching of image areas must also be considered.

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2.2.3. The restoration, conservation and examination of the sixteenth-century prints found on Nova Zembla

Willem P. van Oort, Peter M. Poldervaart and *Judith H. Hofenk de Graaf*

An attempt in 1596 to reach China by ship via the Northern Passage, ran aground on the island of Nova Zembla. The seafarers were forced by the ice to wait out the winter there. Packets of prints, which they had taken with them for trade purposes, were left behind on Nova Zembla after the winter stay. At the end of the 19th century these prints came into the possession of the Rijksmuseum, but caked together into almost solid blocks. In the past decade, various unsuccessful attempts were made to free the prints from the blocks. In 1975-76 attempts were begun anew, under the close collaboration of a scientific specialist, J. Hofenk-de Graaf, and the paper restorers of the Rijksmuseum, finally yielding successful results. Among other things they made use of enzymes in water and alcohol. This experimental method was further developed by the paper restorer P. Poldervaart, who in 1977, in collaboration with the chief restorer of the Rijksprentenkabinet, W. P. van Oort, began the process of separating the prints from their blocks. An extremely intensive and laborious job, that at present is almost completed, has yielded more than 600 prints (by Goltzius, de Gheyn and many others) from which many unknown impressions have come to light.

Introduction

Dutch attempts to find a northern route to Asia in the 1590s were largely stimulated by Southern Netherlanders, notably the merchant B. de Moucheron and the geographer P. Plancius. One of the leading explorers was William Barentsz, whose voyages led to the discovery of Bear Island and rediscovery of Spitzbergen, with the subsequent development of whaling there. He published a map of the North Pole region in 1598 and the account of his explorations ran into many editions in numerous languages.

During the winter of 1596-1597 Barentsz had to remain in Nova Zembla and left a large part of his ship's cargo and equipment behind on his departure. In 1871 the remains of his winter camp were discovered and a Norwegian firm tried to sell some objects from it to the Dutch government. Subsequently an Englishman, C. L. W. Gardiner, recovered a large number of objects, also offering them to the Dutch government. Two small publications were devoted to the finds and in 1885 they acquired a place in the Rijksmuseum, where they were later to be joined by still more objects retrieved by later expeditions. The way in which these were displayed initially expressed their status of national relics. They enjoyed great fame, mainly because of their 'ethnographic' character as concrete objects from the daily life of our forefathers, but, apart from investigations concerning the nautical instruments, little historical research was devoted to the collection as a whole. However, a publication covering all its aspects is currently in preparation.

The finds included a large number of prints on paper and the first publication of 1872 already pointed out that these were intended as merchandise (a comparison has been made with a list of trade goods left by the Dutch at their factory at Patani in

India in 1602, which also included a large number of prints — about 4000 — 5000). The packs of prints acquired in 1871, 1876 and 1892 had in most cases become pulped together into hard, solid masses resembling blocks of papier-mâché because the animal size in the papers had dissolved, penetrated through all the layers and dried, adhering the deteriorated prints to one another *(Figures 2.32* and *2.33).*

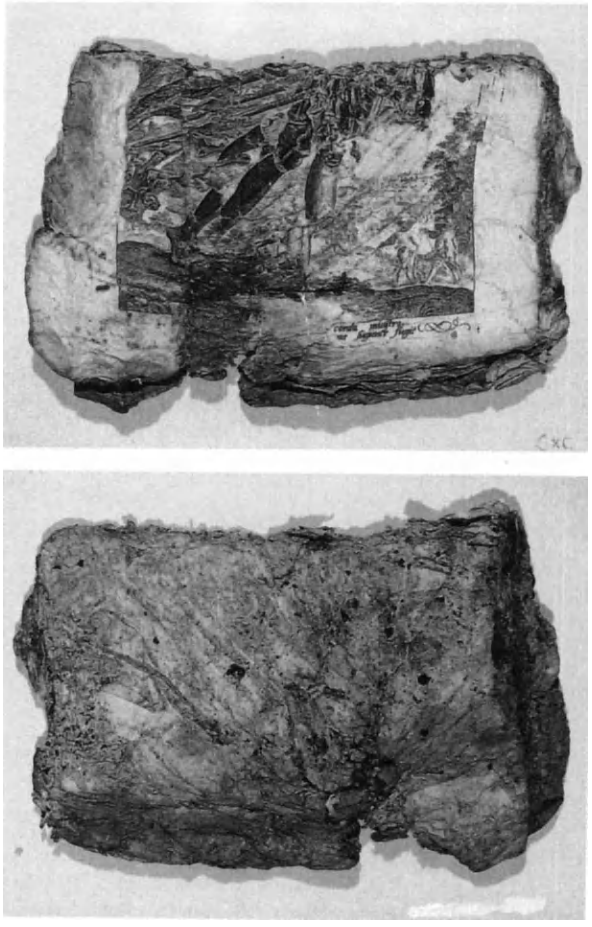

Figure 2.32

Restoration and Conservation of the Nova Zembla Prints

In the 1960s, Ch. Wolff, who was at that time the paper conservator of the Rijksprentenkabinet, had already made attempts to separate the blocks of Nova Zembla prints but these were not continued. In 1975 the Department of Dutch History began seriously organizing a catalogue of the Nova Zembla finds at which time there was a reawakening of the need to separate the individual prints from the adhered lumps so as to be able to identify the artifacts making up this section of the finds.

Figure 2.33

A commission of experts was set up[1], advised by J. H. Hofenk de Graaf of the Central Research Laboratory for Objects of Art and Science, Amsterdam, and decided that experiments should be carried out to see whether it would be possible to separate the prints. As well as Hofenk de Graaf, the paper conservators K. Oldewelt, P. Vlasweld and Ch. Wolff took part in the experiments. These (see below) were carried out in December 1975 and showed that it would indeed be possible to separate the prints but that it would be a difficult and time-consuming job which would need an experienced paper conservator[2]. Because of the magnitude of such a restoration project it could not be carried out by the paper conservators of the Rijksprenten-kabinet because they were already heavily involved in their day-to-day work. Therefore a paper conservator, Peter Poldervaart, was appointed, and he started on the restoration project in September 1977 in the workshop of the Rijksprentenkabinet under the supervision of its head conservator, Willem P. van Oort.

Using the results of the experiments of December 1975 as a basis, Poldervaart further developed the technique for separating the prints. Although the work indeed proved time-consuming, the prints were separated, fragment by fragment, from the solid lumps. About 1000 fragments, including a

large number of smaller fragments, corners of prints, etc., were isolated from about ten lumps.

This first stage of the restoration ended in the autumn of 1979, after which the next stages could be carried out. Further conservation efforts comprised the transfer of the isolated fragments from the Melinex (polyester) support sheets, used during the separation operations, to support sheets of Japanese paper. The fragments were then matched with other fragments of the same print whenever possible. This stage of the project was completed in the summer of 1980. The reconstructed prints and the remaining fragments were then mounted, filed and placed in boxes.

Research and experiment

Preliminary research

The lumps of prints

The prints found on Nova Zembla, as noted above, as well as books and documents had, in most cases, caked together into hard solid masses. The condition in which the artifacts had survived was due to the circumstances to which they had been exposed on Nova Zembla for nearly three centuries — alternating periods of environmental change during which the lumps were either wet or frozen (from 5 °C to —30 °C). During this period the animal glue (gelatine, bone size, parchment size, etc.) used to size the papers penetrated the layers thoroughly, so that the prints became a kind of papier-mâché — solid lumps of fibrous material. At the edges the layers had caked together into a mass of hard paper fibres. A lot of dirt had also accumulated. As evidenced by their compactness, all the stacks of paper must have been under pressure. In the preliminary research and experiments a small lump of prints and a few loose map and print fragments were used for testing and analysis.

Composition of the papers

In Europe, traditionally, handmade paper has been formed by scooping up small quantities of a suspension of fibres in water on the screen of a hand-held papermaking mould. This suspension is evenly distributed on the screen so that when transferred to felts, pressed, separated and dried, a sheet of paper is formed. In order to reduce the porosity of the sheet and to give other desired properties, handmade paper can be sized by immersing in a warm bath of animal glue/size in water (tub-sizing), after which they are dried and pressed. Up to the early nineteenth century this was the principal method of sizing European papers.

At this stage the sheet of paper consists of two different materials: fibres and size. The fibres which constitute the paper proper, in the later centuries of Western European hand-papermaking may be of linen, hemp, cotton or a mixture of these (i.e. until the introduction of other fibres in commercial-level papermaking in the late eighteenth and early nineteenth centuries). They are basically composed chemically of forms of *cellulose*. Sizes consist of animal-derived glues such as skin-glue, bone-glue, fish-glue, etc., which, from the chemical point of view, are *proteins*.

As outlined above, the size of the Nova Zembla prints has penetrated throughout the stacks of paper, thus acting as a binding agent between their layers. In order to separate the individual sheets of paper the size, a proteinaceous material, must be released.

Small samples were taken from different sections of the test lump and tested for the presence of proteins to verify whether the size had indeed penetrated throughout. These samples were examined using thin-layer chromatography, a method used for the detection and analysis of minimum quantities of proteins[3]. The analysis indicated that the whole paper lump contained proteins which confirmed the assumption that the size had penetrated the entire stack of prints and glued them together.

Use of enzymes to facilitate dissolving of the size

Animal glues or sizes such as those mentioned above are soluble to varying degrees in water. It may, however, be a rather laborious process for the conservator to dissolve them as they tend to swell and become a gelatinous mass which can only be removed with difficulty using hot water. It would thus be preferable if the large protein molecules which make up the sizes could be broken down so that they lose their adhesive power and readily dissolve in water. To release the adhered layers of the Nova Zembla prints the use of enzymes was therefore proposed.

Enzymes were formerly called ferments. A well-known example is yeast, used in the production of alcohol. Enzymes are catalysts — compounds which start or accelerate a chemical reaction without taking part in it directly[4]. They are present in nearly every chemical reaction in living organisms. These 'biocatalysts' may speed up many chemical processes quite considerably in spite of very mild environmental conditions such as low temperatures and a neutral pH. Enzymes have so much catalytic activity that reactions may be 100—1000 million times faster than equivalent non-enzymatic reactions.

Apart from the fact that they accelerate reactions, enzymes are characterized in particular by their high degree of specificity. In other words, a given enzyme can bring about the conversion of only a limited number of closely related chemical compounds. For example, one particular group of enzymes facilitates the breakdown of proteins into amino acids, i.e. into the basic elements of all proteins. One such enzyme is trypsin.

In order to separate the individual paper layers of the lumps of Nova Zembla prints the protein elements of the adhesive sizing material had to be broken down for easier dissolution but without, however, affecting the cellulose elements of the paper fibres. The conclusion was reached that the trypsin could be used in dissolving the size as it is specific for the breakdown of proteins and would not harm the cellulose (compound of glucose, i.e. sugars). By developing a method for its use the size could be removed without damaging the paper itself. Another advantage in the use of trypsin is that it is not necessary to raise the temperature, as the desired reactions occur readily at room temperature.

Experiments were accordingly carried out with trypsin and later with the commercial product Biolase G, which contains the same enzymes promoting the breakdown of proteins. In both cases good results were obtained.

The experiment

J. Hofenk de Graaf, in collaboration with other paper conservators, developed the following method based on her preliminary research.

Experimental soaking in an enzyme solution

The lump of paper, placed on a sheet of Melinex (polyester sheet), was immersed in a basin containing a solution of 10g Biolase G enzymes in a litre of de-ionised water in order to break down the size. In practice it proved better to replace half the water of the enzyme solution with ethyl alcohol (ethanol). This made it easier for the solution to reach the core of the solid lump of prints while reducing the swelling of the fibres and retaining better cohesiveness of the paper layers.

After the lump being treated was thoroughly soaked it was taken from the solution, still supported by the Melinex sheet, and then dried with blotting paper until moisture no longer seeped from it.

After the treatment in enzyme solution a mass of fibres was left which was less stuck together — but in which the paper layers also had very little cohesion.

Experimental separation of the prints from the lump

To separate the layers of paper a pasted sheet of Melinex was pressed firmly on the top of the lump. This made the upper surface of paper adhere to the Melinex while the paste reinforced it at the same time. The topmost layer or layers of paper thus stuck to the Melinex were then separated from the rest of the lump very carefully and slowly with a type of palette knife. On the whole it was not possible to detach the sheets of paper one layer at a time because they proved too fragile — two or three together had more cohesion.

Initially, hydroxypropycellulose (Klucel G) was chosen for the adhesive paste. This cellulose product is soluble in ethyl alcohol as well as in water. For this paste application a 6% aqueous solution of Klucel G was used. When the paper on the Melinex had dried, excess paste could be removed with alcohol.

The main argument in favour of this method was that when the paper had dried it need not be moistened again, which was a positive factor considering the fragility of the paper.

After the lump had been separated into small groups of two or three print layers it was possible — when they had dried — to separate them into their individual paper layers using Renova paper impregnated with polyvinyl-acetate. (50% DMS, 50% DM 2). The bi- or tri-layered fragment was placed between two sheets of impregnated Renova paper to which it was then heat-set with a hot iron. The prints whose outer surfaces were thus adhered to the Renova paper then could be separated from each other very carefully. The Renova paper was detached from the prints by putting them in an alcohol bath for 3 or 4 hours.

Experimental methods for the preservation of the detached fragments

The detached fragments were dried on sheets of Melinex onto which they had been adhered. The adhesive could be easily removed with water or alcohol at a later stage.

The detached fragments were then sealed temporarily between two layers of Melinex. Some time after the initial experiments it was found that mould had developed in some of these hermetically sealed bags so that they had to be opened immediately. This is the reason that a number of detached prints and fragments show distinct brown stains.

The experiments proved that many of the lumps of paper could be separated into sheets, although it was doubtful whether this would always be possible, especially in those cases where the lumps had folds and creases stuck together.

The working group furthermore concluded that the restoration had to be carried out by an experienced paper conservator and that it was essential to document the restoration project by means of photographs.

Conservation and restoration of the prints

Separation of the prints

The paper conservator, Peter Poldervaart, was able to start the project on 1 September 1977. In consultation with an internal advisory commission for the restoration (W. P. van Oort, J. P. Filedt Kok, J. Braat and B. Kist), agreement was reached concerning the working method, documentation and photographic recording.

The method used to separate the prints, which — as has been outlined above — was developed experimentally in 1975, was explained and demonstrated to Poldervaart by Hofenk de Graaf. This technique was used when the restoration project was started, but it soon became clear that a number of improvements were possible.

Soaking of the lump in an enzyme solution

It turned out that the Biolase G enzymes (which Hoechst at that time had taken off the market) browned the solution in which the lump was 'soaked' and hence also the lump itself. Consequently the Biolase G enzymes were replaced with Maxatase enzymes (Gist Brocades), which react in a similar way but do not stain the solution.

Moreover, a different method was found to soak the lump. Since each day the lump being treated was immersed and left to soak and then retrieved from the solution to be dried, it started to fall apart after a few of these cycles. Another disadvantage was that a new enzyme solution had to be prepared each day since its ethyl alcohol component evaporated. It was therefore decided to keep the solution in a closed litre bottle. The top layers of the lump — which was placed on a Plexiglas sheet — were then soaked using a tuft of cotton wool *(Figure 2.34(a).*

Once applied to the top of the lump, the solution had to be left to soak in for about 30 min to allow the enzymes to react. Excess liquid was then removed with cottonwool so that the area of the lump under treatment was neither *too wet* nor *too dry (Figure 2.34(b).* This was very important, since on the one hand the topmost sheet of the lump had to remain attached to the applied sheet of Melinex (with the help of the Klucel G paste), while on the other it had to be detachable from the rest of the lump. To avoid the moistened lump drying during the night, it was covered with waxed paper after the day's work.

Since, according to theory, enzymes react better in a warm solution, a method was tried in which the bottle with the solution was heated *au bain marie.* The lump was then moistened with the warm solution, but as the lump was colder the solution cooled down immediately. To get around this problem the lump was gently heated with a hair dryer. However, even this method did not yield the desired result and proved to be far too time-consuming and cumbersome, so it was discarded.

Separation of the individual prints from the lump

The technique mentioned above by means of which the topmost layer (or layers), after release with enzymes, was detached with the help of a thin knife and a sheet of paste Melinex became refined to such a degree that it was possible to detach one sheet at a time instead of two or three sheets, as had been the case at the experimental stage. A different adhesive and finer tools were ultilized. It was found that the Klucel G paste did not adhere sufficiently, so it was decided to use methylcellulose MCP 400 in an 8% solution, which adheres better to the fibres. It also became clear from the start that tools finer than an ordinary palette knife were needed. Various stainless steel 'palette knives' used by dentists proved to be the answer. These were used both to detach the print layer from the lump and to press the detached paper carefully to the pasted Melinex so that no pieces of paper or constituent fibres were left behind *(Figure 2.34(e)-(b).*

During the course of the project the following problems occurred — among other things. The most difficult and time-consuming part of the operation was the detaching of individual sheet layers, as it was hardly possible to ascertain whether one was handling a single sheet or several sheets at once. This was particularly difficult when successive layers of prints had identical images and were aligned in a neat stack. There was even more of a problem when the prints were folded and creased or when the paper was crushed to such an extent that only loose fibres remained. One also had to be careful not to split one sheet into two (in the plane of its image surface).

However, with experience, the conservator was able to see from the colour, by holding the corner of the split paper against daylight, whether half a sheet or one or more sheets were involved. If too much or too little had been detached, another corner of the lump was started on.

When splitting the print layers the quality of the paper had to be taken into account; some prints had been printed on thicker and others on thinner paper. The most difficult parts to separate proved to

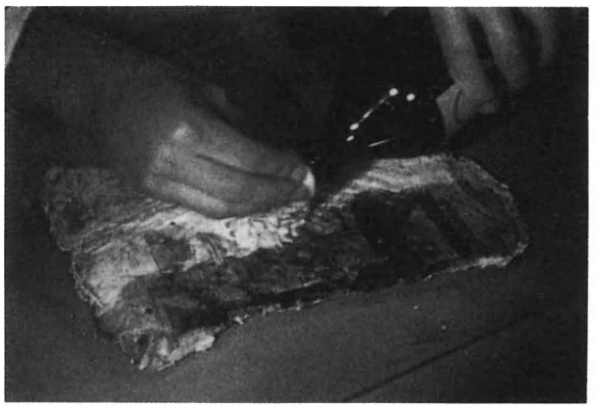

Figure 2.34(a)

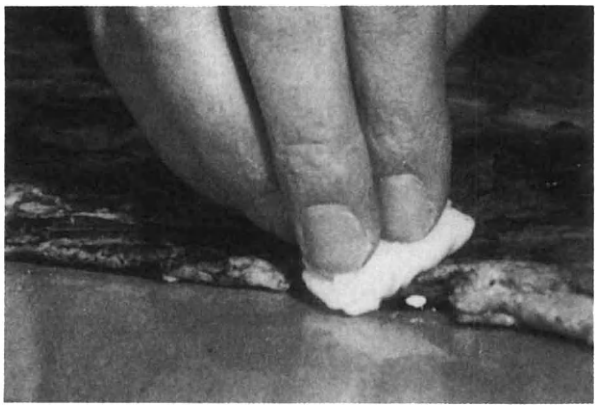

Figure 2.34(b)

be the marginal areas of the printed sheets of paper, since there is no printing ink on these parts. (It was also observed that, since the printing ink constituted some sort of physical buffer layer, the fibres of the well-inked parts had not been crushed so badly. On the other hand, when printing ink was involved the fibres disintegrated more easily.) The top and bottom layers of the lump were also difficult to split since these parts had suffered most damage and often had caked together into a black pulp.

The number was pasted immediately on the Melinex sheet supporting the detached Nova Zembla sheet or fragment. Each time a sheet was detached, it was photographed with the relative number (e.g. CCIII-11) while at the same time the lump was photographed with the next sheet number (e.g. CCIII + 12, i.e. the lump before the twelfth sheet was detached).

During the first stage of the restoration the conservator took photographs with a temporarily

Figure 2.34(c)

Figure 2.34(d)

Documentation and photographic recording

Before the restoration work began the Photographic Service of the Rijksmuseum had photographed all the lumps and fragments, including those which had been detached during the experiments. These photographs were numbered with Roman numerals (e.g. CLXXV, CLXXVI, etc.). Although this was a very complicated system, the numbering was continued in this way. The number of a given lump (e.g. CCIII) was given to each sheet that had been detached from that lump, followed by the serial number (Arabic numeral) in the sequence of detached sheets. To illustrate this: No. CCIII-11 refers to the eleventh print that has been detached from lump CCIII (starting from the topmost sheet).

fixed camera installation (Nikkormat camera). Later on photography was done with a permanent installation set up especially for paper conservation purposes *(Figure 2.35)*.[5]

The photographs were filed in folders and constituted, besides an accurate record of the restoration process, an invaluable aid in the reconstruction of the original sequence of the prints.

The conservator kept a logbook of the whole process in which problems and details were recorded on a day-to-day basis. By the autumn of 1979 all the lumps, fragments, etc. had been separated and fixed on Melinex (even small pieces of the Nova Zembla paper finds have been separated into their individual paper layers — often revealing corners of prints). In many cases it also proved

Figure 2.34(e)

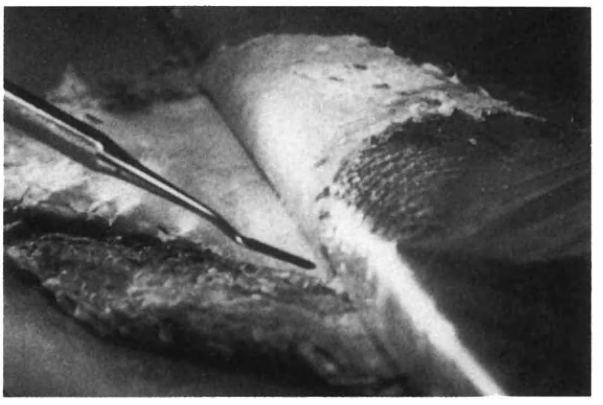

Figure 2.34(f)

possible to detach and split fragments treated during the experiments of 1975 still further.

Conservation, mounting and storage of the detached prints

To conserve the detached prints and fragments it was thought inadvisable to keep them permanently adhered to Melinex sheets. The papers attached to their supports were still so fragile that they were difficult to handle, and it was feared that in the long term parts might come loose. It was therefore decided to transfer the detached sheets to a Japanese paper support. The sheets were then, insofar as reconstruction permitted, combined with fragments of the same print and placed in acid-free paperboard covers and stored in boxes.

Figure 2.34(g)

Transfer of the prints from Melinex to Japanese paper

At first it was not easy to remove the prints from the Melinex because the dried MCP adhesive could not be dissolved in hot water or in methanol (methyl alcohol) (which is, moreover, hazardous to health). However, because this adhesive had formed a film between the Melinex and the print, a thin palette knife could be inserted between them and the dry print detached. The following operations were then carried out:

(1) The detached print was placed on Melinex with the adhesive side up;
(2) The whole was moistened with water with a fixing sprayer and soaked for about 15 min;
(3) After a second Melinex sheet had been placed on the print the whole sandwich was turned upside down;
(4) The first sheet of Melinex was then removed and the fibres adjusted into their correct place;
(5) The Japanese paper pasted with starch paste was placed down onto the back of the print;
(6) After excess moisture had been removed with a sheet of filter paper the whole was flattened with a roller;

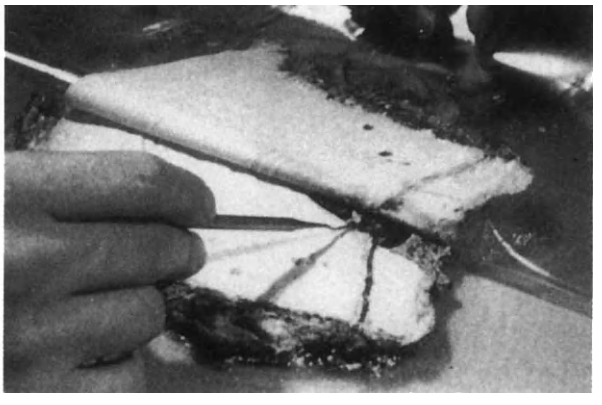

Figure 2.34(h)

(7) The whole was then turned over again and the second sheet of Melinex removed, after which the remaining MCP adhesive was removed with a palette knife.

It was found, however, that when a print detached from Melinex was moistened with *cold* water the adhesive dissolved. Therefore the process could be simplified as follows:

Figure 2.35

(1) The face of the print was pasted onto Melinex, then thoroughly moistened with cold water with a fixing sprayer (at a maximum water temperature of 20°C) and left to soak for about 15 min *(Figure 2.36(a))*;

(2) Excess water was removed with a tuft of cottonwool and the fibres were pushed into the right positions *(Figure 2.36(b))*;

(3) The Japanese paper, moistened with a fixing sprayer, was pressed onto the whole *(Figure 2.36(c))*;

(4) This was then turned over and the Melinex removed *(Figure 2.36(d))*;

(5) Since very often no adhesive was left in the fibres of the paper, additional MCP adhesive was pasted on to the face of the print *(Figure 2.36(e))*. The adhesive passed through the fibres and stuck to the Japanese paper lining. In this way the print was also consolidated sufficiently at the same time.

Figure 2.36(a)

Figure 2.36(b)

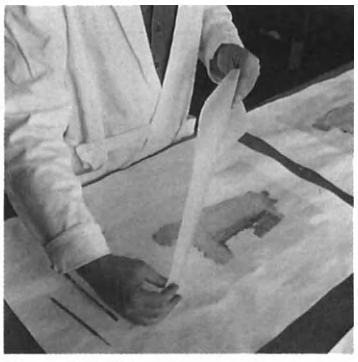

Figure 2.36(c)

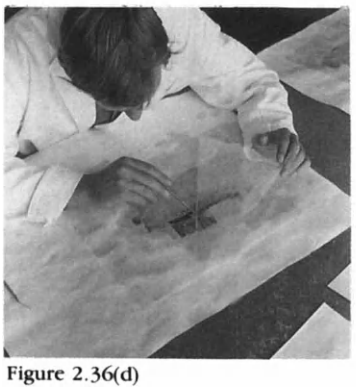

Figure 2.36(d)

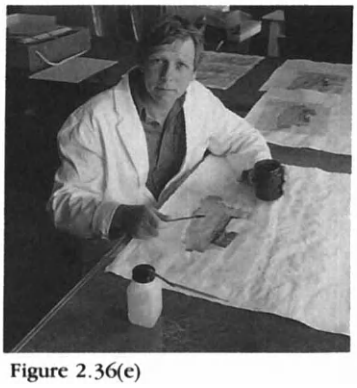

Figure 2.36(e)

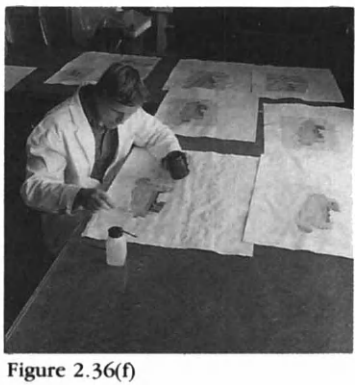

Figure 2.36(f)

Reconstruction of the prints and their sequence in the stacks(s) of prints taken to Nova Zembla

When the lumps came into possession of the museum in the nineteenth century they were filed under three numbers. Before 1977, when a start was made on the separation of the prints, there were ten larger lumps, consisting of complete or half prints

and twenty small lumps which consisted mostly of corners or edges of prints.

Following the separation process, several lumps proved to consist of halves of prints. To match halves and fragments was a time-consuming occupation. This was done mainly by the art historian on the team assisting the restoration, on the basis of the photographs taken during the separation of the prints. The prints were first identified whenever possible, and in the majority of cases this could indeed be done. In most instances, complete prints of the same engravings existed in the collection of the Rijksprentenkabinet.

With the help of lists of halves of prints and/or fragments in the various lumps it proved possible to reconstruct most of the prints with fair certainty and to establish the original sequence of prints in the stack(s). This was also possible as the same sequence of upper and lower halves of prints was found in two different lumps, e.g. seven prints of the *Adoration,* then seven prints of *Virue Conquering War,* then seven prints of *Judah and Tamar,* etc.

Even in the smaller lumps which only contained corners, the same sequence as in a larger stack was often found. At times a stack of the same prints had been tied with a string which, when loosened, remained on the topmost print. In many cases a print could be reconstructed utilizing two surviving halves or several different pieces.

Things became more complicated when the prints had been folded or turned upside down. For example, among the prints of *Tabula Cabetis* by Galle, six folded prints of the right side had been mixed up with seven folded prints of the left side. Another problem was that reconstruction of the sequence of the whole series of prints and of the sequence of prints used in the initial 1975 experiments was hampered by the lack of notes at the experimental stage.

A number of loose fragments from this stage have been left over. It is thought that they had originally been placed above the lumps XCIX and XCVII (with the left and right halves, respectively, of the *Great Lion* by De Gheyn) and beneath the lumps XXCIV and CLXXXIII (with fragments of the *Tabula Cebetis).*

Apart from that, so many links can be found between the various lumps that it is easy to presume that initially there must have been one or two large stacks of prints.

Matching the fragments and the filing of the reconstructed prints

On the basis of the reconstruction outlined above, fragments which were clearly part of the same print were placed side by side and matched up by the conservator. It was decided to place all the fragments of each print on their own Japanese paper support side by side on a sheet of acid-free board.

Before the prints were fixed, any watermarks were traced over a light box *(Figure 2.37).*

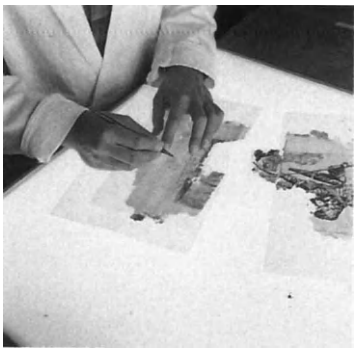

Figure 2.37

In order to give an idea of the original prints, the fragments were placed as close as possible to each other. This was achieved by placing the fragments lined with Japanese paper over a light box so that they could be aligned as much as possible. The overlapping areas of Japanese paper were then cut off with a fine knife *(Figure 2.38).* The next step was to attach the fragments in their appropriate arrangement to acid-free board using strips of Japanese paper and paste. A second sheet of acid-free board, serving as a cover which folds back, was then attached to the first.

Figure 2.38

On the outside of this cover sheet the inventory numbers and the numbers of the various fragments from which the sheet has been reconstructed are noted. The prints are stored in boxes in the same sequence as will be used in their description in the catalogue of the Nova Zembla collection.

Description of the prints

The description of the prints in the 1602 list from Patani (see above) are too summary to allow of identification, so the Nova Zembla find provides the first opportunity of studying in the original a

collection of prints sent to the East as merchandise. What percentage of the whole the finds represent is unclear, although the fact that only small corners of some large prints were found showed that parts, at least, have been lost. Nor is it clear how far the remaining prints are a representative collection. Around 400 impressions were found of 150 different prints. With costume prints, landscapes, classical and biblical themes, emblematical compositions and secular subjects, the collection offers a limited but reasonable cross-section of the range of prints made around 1590, with the exception of portraits. The 1602 list is much larger, showing an even greater variety of subject matter, especially in respect of secular themes, and including some portraits of historic figures.

The prints still retain the wide margins, which have normally have been lost in the course of time, and this suggests that they were brought directly from a publisher or dealer and that nothing was done to them. No particular system could be discerned in the order of the prints in the stacks.

The majority of the prints were made in the North Netherlands around 1590, the most notable being a large group by the Haarlem school of engravers around Hendrik Goltzius. The finds, in fact, yield much about the early stages in the development of the school. There are no original engravings by Goltzius but a number of copies exist, mostly in reverse: a complete series of the *Roman Heroes* of 1586, the *Standard-bearer* and *Infantry Captain* of 1587, *Hercules* of 1589, *Penitent Magdalene* of 1582, *Susanna* of 1583 and *Adam and Eve* of 1585. *(Figure 2.39)* Two prints that probably also belong to the Goltzius school are *Judith and Tamar* and a hitherto unknown composition, *Virtue Conquering War.* None of these prints bears a signature, so they are probably all pirated copies.

Figure 2.39

More significant artistically is a group of engravings by Jacques de Gheyn II, including a number of important originals. This group includes copies of the complete series of *Officers and Soldiers from Rudolph II's Bodyguard* of 1587, at least six complete sets of *The Four Elements,* several impressions of *Acis and Galatea* and more than 27 examples of the imposing folio *Great Lion (Figure 2.40).* This Northern Netherlandish group also includes at least seven sets of *The Story of Tobias* after Carel van Mander attributed to Z. Dolendo, while two previously unknown prints in a closely related style are *The Judgement of Paris (Figure 2.41)* and *The Reconciliation of Jacob and Esau.*

A smaller, but still important group of slightly earlier South Netherlandish prints begins with the remarkable *Tabula Cebetis* of 1561 by Ph. Galle, of which there are certainly seven or eight examples. It also includes a complete series of 24 *Landscapes in the Environs of Brussels* by Hans Collaert, two sheets from a series of *Roman Emperors* by Adrian Collaert, two series of costume prints by Abraham de Bruyn and a number of unsigned prints possibly of South Netherlandish origin *(Figure 2.42).*

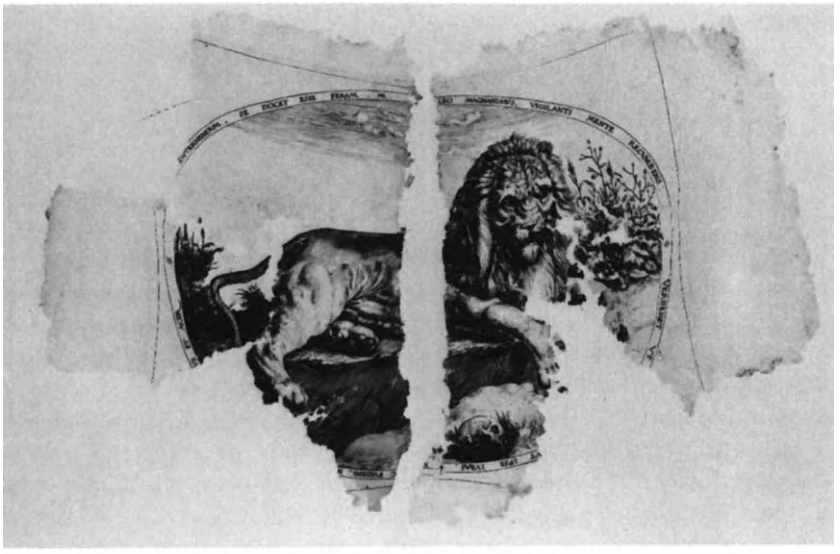

Figure 2.40

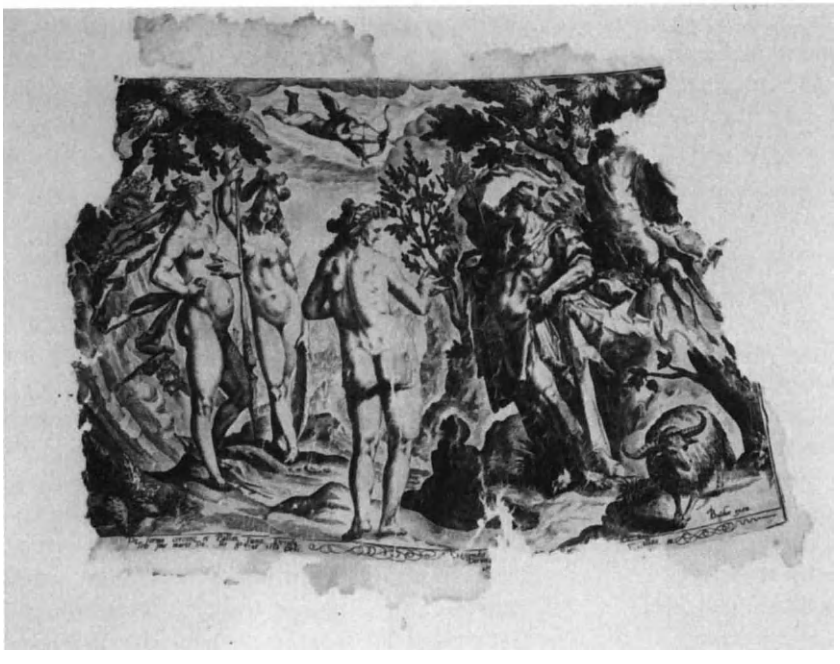

Figure 2.41

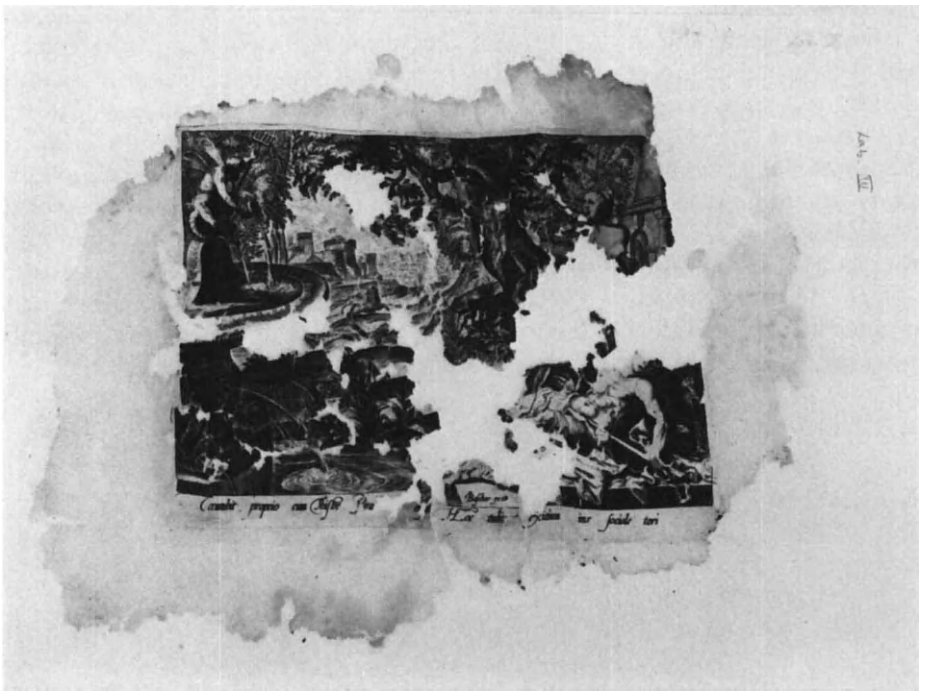

Figure 2.42

The majority of prints bear the address of Isaac de Bosscher, about whom nothing is known, although much argues that he was of Amsterdam. In the case of De Gheyn, whose earliest prints were published by Goltzius, the co-operation with de Bosscher seems to have started in 1558 and continued until 1593 (prints of 1593 and 1595 by De Gheyn were published by Razet). De Bosscher also published Van Mander's *Tobias* series and some of the Goltzius copies, while the *Tabula Cebetis* also bears his address. The prints by Collaert still bear the old address, but they were reprinted in Amsterdam later. Since prints without De Bosscher's address are mixed up in the stacks with those with it, it seems obvious that all the prints were bought at the same time in his shop or from a dealer allied to him. The *en bloc* purchase may, in fact, have had to do with his circumstances, since his co-operation with De Gheyn ended at around the same time.

Of the article by J. Braat, J. P. Filed Kok, P. Poldervaart and J. H. Hofenk de Graaf published in Dutch in the *Bulletin van het Rijksmuseum,* **28**, 43-79 (1980), Chapter 2 concerning the restoration and conservation of the prints has been translated here in full by J. Poldervaart and L. Faili. Of Chapters 1 and 3, only the summary by Patricia Wardle is given here. The article has been written in close consultation between the authors.

All the photographs, with the exception of *Figures 2.34-2.38,* were made by the Photographic Service of the Rijksmuseum. The photographs for *Figure 2.34* were taken from the film *Prints Off the Ice* (an 18-mm colour motion picture; duration 30 min) by W. Stam (Photographic Department, Foundation Film and Science, Utrecht). The photographs for *Figures 2.35-2.38* were taken by G. van Rossum-Bauknecht (Conservation Workshop, Rijksprentenkabinet, Amsterdam).

Acknowledgements

The restoration, conservation and research was carried out in close consultation between the restorer P. Poldervaart and the restoration commission (see note 1), after preliminary research in which participated the paper conservators P. Vlasveld (at the time at the Municipal Archives, Delft; at present at the Municipal Archives, Amsterdam), K. Tilanus-Oldewelt (at the time at the Rijksprentenkabinet) and Ch. Wolff (Central Laboratory).

Notes and References

1. On this commission, set up to plan the restoration of the Noya Zembla papers, sat J. H. Hofenk de Graaf (Central Research Laboratory for Objects of Art and Science), G. de Graaf (Public Record Office, Utrecht), A. R. A. Croiset van Uchelen (University Library) and W. P. van Oort, J. P. Filedt Kok, J. Braat, B. Kist and W. H. Vroom (all of the Rijksmuseum, Amsterdam). It met twice, once on 17 November 1975 and on 9 February 1976.

On 9 February 1976 it was decided that the lumps of prints were to be restored and a commission of experts was established in which participated the persons from the Rijksmuseum mentioned above.

2. In January 1976 two reports were made on this experimental research: 'Research for the restoration of the Nova Zembla papers', by J. H. Hofenk de Graaf, and 'Work report' by P. Vlasveld which formed the basis for the decision taken on 9 February 1976 (see Note 1).
3. On the subject of thin-layer chromatography see: Roelofts, W. G. Th. (1972), 'Thin-layer chromatography. An aid for the analysis of binding materials and natural dyestuffs from works of art', *Report,* ICOM Congress, Madrid.
4. On the use of enzymes see: van Oss, J. F. and van Oss, C. J., *Warenkennis en Technologie,* Antwerp (1957). Vol. III, pp. 411-429 (1974). 'The use of enzymes for restoration purposes', *Archives et Bibliothèques de Belgique,* Special Issue No. 12 *(Etudes concernant la restauration d'archives, de livres et de manuscrits),* Antwerp, pp. 235-241; Wendelbo, Ø., (1975). 'The freeing of papyri from cartonnage', *Restaurator, 2.* 52-59 See also Hofenk de Graaf, J. H. (1975). 'The use of enzymes for the restoration of art objects', internal publication, Central Research Laboratory for Objects of Art and Science, Amsterdam.
5. G. B. H. Bijl, head of the photographic workshop of the Rijksmuseum, was consulted for the setting up of the temporary as well as the permanent camera installation. The permanent camera installation of the restoration workshop of the Rijksprentenkabinet was set up in the Rijksmuseum. A Cambo-RTM camera column and two sets of halogen lamps fixed on Durst-Rebel adjustable arms were used. The black and white films (Kodak Panatomic X) were developed and printed by the firm of J. G. Olsthoorn in Amsterdam.

2.2.4. The conservation treatment of a collage: Man with a Hat, by Pablo Picasso

Antoinette King

The condition of this collage of newspaper and blue laid rag paper with Conte crayon and ink on a laid Ingres paper support, dated sometime after 3 December, 1912, had deteriorated dangerously by 1973. The Ingres paper support was covered with large dark brown discolourations. There had been several attempts to locally bleach these stains with various chemicals. Consequently the paper was splitting in all these areas. The entire support was extremely brittle, severely cockled and creased, and discoloured by light. The collage papers were separating from the support and pulling apart.

An attempt to analyze the nature of the discolourations was made by non-dispersive X-ray analyzer. After further analyses and consultation with curators, treatment was undertaken. The papers were separated and the discolourations on the support were removed. The papers were lined and the collage reassembled in its exact original configuration.

The papier collé, *Man with a Hat,* by Pablo Picasso, winter 1912-1913, has already had an extensive history of conservation treatments. This history is, in certain ways, evidence of continuing problems in paper conservation.

Acquired by the Museum of Modern Art in 1937, this work has always been considered an important one, and therefore has been exhibited frequently in spite of its poor condition *(Figure 2.43).* By 1972, periodic inspection of the collage, at that time hanging in the gallery, revealed that the rate of deterioration was accelerating. Concern became alarm when, in the span of a single day, several new tears on the edges were observed to develop. At this time, the object was brought to the paper conservation laboratory for examination and possible treatment.

The papier collé is composed of two pieces of newspaper and one piece of blue rag paper, glued to a support of Ingres laid paper. The design materials are charcoal and black ink.[1] The Ingres support was disfigured by blotchy, purplish-brown discolourations distributed over the entire surface *(Figure 2.44).* In addition, there was considerable cockling in the support, especially on the left, where the cockles radiated through the black ink area. The cockles were creased from having been pressed against the glass in a previous framing.

Differences in expansion and contraction of the different papers over the work's long history had resulted in a dangerous tension between the blue paper and the newspaper, and between the newspaper and the Ingres paper. There was also uneven loss of adhesion between the collage elements and the support, resulting in the support bubbling up on the verso *(Figure 2.45).*

Previous conservation treatments had been directed towards the discolourations. The first of these was a very careful, thoughtful, well-documented treatment by Evelyn Ehrlich at the Fogg Museum of Art, Boston, in November 1941 *(Figure 2.46).* At that time the discolourations were successfully eliminated by brief local application of hydrogen peroxide *(Figure 2.47).* However, in the condition and treatment report it was noted that 'complete correction would be less successful [than an overall treatment]. Discolourations corrected in

this way are also more likely to reappear.' Correspondence of 1944, three years later, mentions the reappearance of the discolourations.[2]

The picture was treated again in 1948 at a renowned New York restoration studio. There is no record of this treatment other than the letter from the Museum which authorized it. Presumably either the discolourations were not decolourized at this time, or they were, but again reappeared.

By the late 1960s the picture again looked as it does in *Figure 2.43,* disfigured by the discolourations. Further attempts to remove the discolourations, this time in the Museum of Modern Art paper conservation laboratory, included local application of chloramine-T, with local rinsing. Nothing tested could even reduce the discolourations.

During the 1972 examination, possibilities of investigating the nature of the discolourations were discussed with Warren Falconer, Head of Physical and Chemical Research at Bell Laboratories, who was scientific adviser at the time, and Edward Sayre of Brookhaven Laboratories who suggested talking to William Young, then Head of the research laboratories at the Boston Museum of Art. The picture was taken to the laboratory at the Boston Museum in order to identify elements in the stains and the surrounding paper by non-dispersive X-ray analysis, a method chosen because it did not require physical sampling. Potassium was found in the stain and also in the paper, possibly indicating a potash alum sizing.

Of particular interest was the amount of iron in the discolourations relative to the amount in the undiscoloured area. A test with 2% acetic acid had decolourized part of one discolouration, suggesting that there was an iron component. A polaroid photograph taken from the display screen of the multi-channel analyser shows a higher iron peak in the surrounding paper compared with the iron peak in the discolourations, indicating less iron in the discoloured areas than in the undiscoloured areas *(Figure 2.48).* Young said at the time that 'as this is quantitative, it would indicate that perhaps the iron has either been destroyed by the mould growth, or that the stains have been treated locally and the iron has been extracted from these areas'.[3]

Further analysis included sampling of a discoloured area for examination by polarized light microscopy. Although the fibres appeared distorted, no major damage to the cellulose structure was evident.[4] Surface pH readings taken with a ceramic tip electrode[5] on several discolourations showed a range between 4.9 and 3.9. The surface pH of the Ingres paper was about 5.2 This was as far as we could go in our investigation of the nature of the discolourations.

Throughout its conservation history, separation of the pieces of the papier collé for overall treatment of the Ingres support had never been seriously considered. The danger of losing alignment of the collage elements was too great. By 1972, however, the residual chemicals from the previous local treatments had caused severe deterioration of the paper, resulting in tiny tears within each discoloured area *(Figure 2.49).* In addition, the entire support paper was extraordinarily brittle and discoloured by light. In view of the extreme fragility of the Ingres paper support and the splitting and tearing caused by residual chemicals, possibly accelerated by light, conservators and curators decided that an overall treatment should be undertaken if possible. It was thought that the picture might soon cease to exist without it.

The picture was examined further in MoMA's laboratory to determine the feasibility of separating the papier collé elements, treating them separately and then reassembling the structure. The animal glue used for the papier collé was tested with moisture and found to be readily soluble. Testing removal of the collage elements was only the first hurdle.

The next was determining whether the charcoal design could be fixed, as was necessary before the Ingres paper support could be washed. Normally use of fixatives on design elements is not considered, but, as mentioned, conservators and curators felt the condition of this picture warranted more radical treatment than usual. After a number of tests, it was found that the design on the support could be fixed with a 2% solution of Acryloid B72, a methyl acrylate methacrylate copolymer, in xylene, applied to the design lines with a fine brush. This did not at all change the appearance of the charcoal when viewed without magnification. (Today, eight years later, when the picture is examined closely, there is a very slight warmth to the thinner lines, a very slight brownish cast.)

Tests for a possible fixative were done before any treatment was undertaken. The collage elements were removed after the position of each was recorded with minute pencil marks on the support. The design was fixed after the glued pieces were removed from the support. Only at this point was it clear that the Ingres paper could be washed.

Careful measurements of the dimensions and alignments of the papier collé were made in addition to documentation photographs. An upright wood strainer was constructed and the picture was hinged to it *(Figure 2.50).* The hinges were mulberry paper with water-torn edges, adhered to the papier collé with pure wheat starch paste, and to the wood with polyvinyl acetate copolymer emulsion (Jade No.

403). Wynne Phelan, who collaborated on the treatment of the collage, lightly steamed the verso, just in back of the glued pieces *(Figure 2.51)*, while they were lifted off the recto intact *(Figure 2.52)*. The adhesive was so readily soluble that the papers came off almost instantly. At this point, it was important to keep the pieces together if possible in order not to lose their alignment. The bottom piece was so loosely attached, however, that it separated with a little moisture.

With the papier collé elements removed, the different types of discolourations of the support were revealed *(Figure 2.53)*. The support paper was discoloured from light in areas which had not been covered by the collage elements, and was very discoloured from acidity and coloured extractives in areas which had been covered by the newsprint pieces. The lighter lines within the area of discolouration from the newsprint corresponded to the charcoal lines on the surface of the newsprint. Here the support paper was relatively undiscoloured by the newsprint, protected, as it were, from the action of light, all the incident light having been absorbed by the charcoal *(Figure 2.54)*.

The underdrawing of the *Man with a Hat* could also be clearly seen after the glued pieces had been lifted off the Ingres support *(Figure 2.53)*. It is particularly interesting to note the complete changes Picasso made in the drawing on the larger newspaper piece, evidence of the way he worked: 'Starting off with a drawing, which he used as a direct stimulus for the creation of a papier collé . . . First papiers collés, done towards the end of 1912 in Nov. or Dec., to the best of our knowledge — started off with what are in fact paintings created out of collages, and went on to works in which an armature was drawn in, which carried on a dialogue, as it were, with pieces cut from newspapers or coloured paper . . .'[6] Picasso's studio, boulevard Raspail, 1912-1913, shows works pinned to the wall *(Figure 2.55)*. On the bottom, second from the right, one can see an idea similar to the underdrawing of *Man with a Hat* in the central lines on the viewer's right not covered with paper.

The support paper was removed from the strainer, washed in successive baths of deionized water to remove residual chemicals, and air-dried on a blotter to retain the cockling. The paper felt stronger and more flexible after washing. At this point it was intended to remount the collage elements with little or no attempt to relax and flatten the support; we were concerned that such an attempt would alter the dimensions and alignment of the papier collé.

Further tests were made on the discolourations, disclosing that only chlorine dioxide (sodium chlorite acidified with formaldehyde) would decolourize them.[7] The support paper was bleached for 10 min in a 1% solution of chlorine dioxide in deionized water and rinsed in successive baths of deionized water, until no chlorine remained in the baths.[8] This treatment eliminated the discolourations but did not affect the soft buff tone of the paper *(Figure 2.56)*. After bleaching, the recto was still somewhat darker than the verso, the overall light discolouration not having been completely affected by the treatment. The overall discolouration from light had had greater effect on the recto, while the verso was not appreciably discoloured. Allowing some of the overall discolouration of the support paper to remain preserved the aged colour balance of the papier collé, since cleaning of the collage elements was precluded. This was partly because they might have expanded or contracted in the process, but more importantly because the original colour of the newsprint could not be determined.

There is scholarly discussion about what tonalities the newsprint pieces might have had when Picasso used them for his papiers collés. Obviously, the newsprint on this picture must now be discoloured by light because the background paper is. Unfortunately, the glue discolouration on the verso of the newsprint obscures the usual clue to its original colour *(Figures 2.57* and *2.58)*.

Margaret Miller established and Robert Rosenblum confirmed that the newspaper used for the *Man with a Hat* was *Le Journal* of 3 December 1912.[9] There are several other Picasso papiers collés using this same newspaper.[10] A comparison of the aged tonalities of these newsprint pieces might lead to some conclusions *(Figure 2.59)*. The newspaper in the papier collé is from *Le Journal* and is dated 15 March, 1913. Its tonality (somewhat orange) is quite different from the newspaper from *Le Journal* dated 3 December, 1912 (a somewhat cool light brown), but it is the same as the orange tonality of the newspaper from *Le Journal* dated 4 December, 1912, used in the papier collé, *Table with Bottle, Wineglass and Newspaper,* Paris, autumn-winter 1912, Musée National d'Art Moderne, Paris.

There is no doubt that these particular newspaper pieces have discoloured considerably since Picasso used them for these papiers collés, which have often been exhibited. They would probably not have discoloured so much in the short time between the publication of each newspaper and the creation of each papier collé. The question remains whether there were differences in hues or tonalities among the various newspapers when they were used originally. Some were probably already slightly aged before use. Are there differences in

manufacture (wood types, sizing, etc.), which might have caused them to have warmer or cooler, darker or lighter, tonalities when Picasso chose them for his works? Or were they exposed to different environmental factors before use? Possibly these slight differences, if they existed, might occasionally have dictated which pieces would be chosen for a given work.

Picasso did keep newspaper collections in his studio for his work. John Richardson has written that he was with Picasso about twenty-five years ago when the artist decided to go through a large group of portfolios, few of which had been opened since 1939, some not since 1914. One of these portfolios contained old newspapers. (Another contained beautiful papers from eighteenth-century Italy and nineteenth-century Japan. 'Far too good to use,' said Picasso.)[11]

The oldest newspaper he used for papiers collés was *Le Journal* dated 28 Mai 1883. Several papiers collés done in the spring of 1913 at Ceret use this newspaper. It is a cool, buff brown, closer to the colour of the newspaper in *Man with a Hat* than that of *Bottle of Vieux Marc, Glass and Newspaper.* The same colour and tonality can be seen in *Head of a Man (Figure 2.62),* and *Guitar, Newspaper, Wineglass and Bottle,* in the collection of the Tate Gallery, London, both of which have the 1883 newspaper. The conditions of storage of the 1883 newspaper prior to its acquisition by Picasso are unknown. Also, it has not yet been possible to analyse the fibres.

There is evidence of careful storage and the resulting fresh appearance of the newspapers other than the portfolios viewed in Picasso's studio. One of the papiers collés found in Picasso's studio at his death was *Table with Bottle,* dated winter 1912-1913 *(Figure 2.63).* An entire newspaper was used for this picture. The page entitled 'La Semaine Economique et Financière' comes from *Le Journal,* probably that of 8 December 1912, judging by the stock exchange report headed 'Coulisse' (the outside market) which includes two dates, 30 November and 7 December, and by the statement that the London conference would open in a few days (this conference began on 16 December 1912).[12] The date of this relatively undiscoloured paper is only five days later than that used for the *Man with a Hat* (3 December 1912). However, in this picture Picasso had reversed the internal relationship of his papier collé, using newspaper as a background. Therefore, he may have wished this newspaper sheet, used as a background, to be fairly white in appearance.[13]

The glue remaining on the reverse of the cut paper pieces was removed with moisture and cotton swabs. Tiny tears were mended with a fine mulberry paper and pure, thin, wheat starch paste. The support and all the collage elements were sprayed many times on the verso with calcium bicarbonate solution in an attempt to neutralize the acidity and possibly to leave some alkaline buffer in the paper without raising the pH above neutrality, which might risk further darkening of the newsprint. Spraying the verso was chosen to avoid possible deposition of carbonate particles into the fixed design layer, which might happen if the papers were sprayed on the recto or immersed in a bicarbonate solution. The surface of the support after bleaching and rinsing was pH 5.2. It was only pH 5.6 after the bicarbonate treatment. The pH of the blue rag paper was not determined. The newsprint pieces were raised to pH 5.5-6.0 (readings taken in different areas) from pH 3.9.

The blue rag paper and the larger piece of newsprint paper, still joined together, were lined with one sheet of mulberry paper buffered with calcium carbonate, with water-thin, pure wheat starch paste as the adhesive. As much moisture as possible was taken out of the mulberry paper by laying it on blotters after the paste was applied. However, the two cut pieces still expanded substantially. We had intended to dry them between blotters with little or no pressure, but due to the great difference in expansion of the two papers, the decision was made to dry the lined pieces on the drying screen, to avoid creasing *(Figure 2.60).* This did not prove satisfactory either, so the papers were removed from the screen while still damp. The lining was removed with very slight moisture, and the papers separated with slight moisture applied with cotton swabs. Measurements were checked and it was found that the newsprint was the same, while the blue rag paper had expanded 3/8 in.

This extreme reactivity to moisture explained the extensive cockling on the proper left of the papier collé support. The blue paper must have expanded when the glue was applied, been glued down in its expanded state and contracted on drying more than the support, causing cockling which was probably not anticipated by the artist, and which undoubtedly worsened with time. Pressure against glass in a previous framing had compounded the problem.

Pierre Daix said that Picasso had 'mastered a new system of equivalences: the different materials used for papiers collés created the same kind of discontinuity as that which exists between different planes in actual space'.[14] Here it almost seems as if the continuing responses of the materials themselves were carrying that formal idea to a logical conclusion.

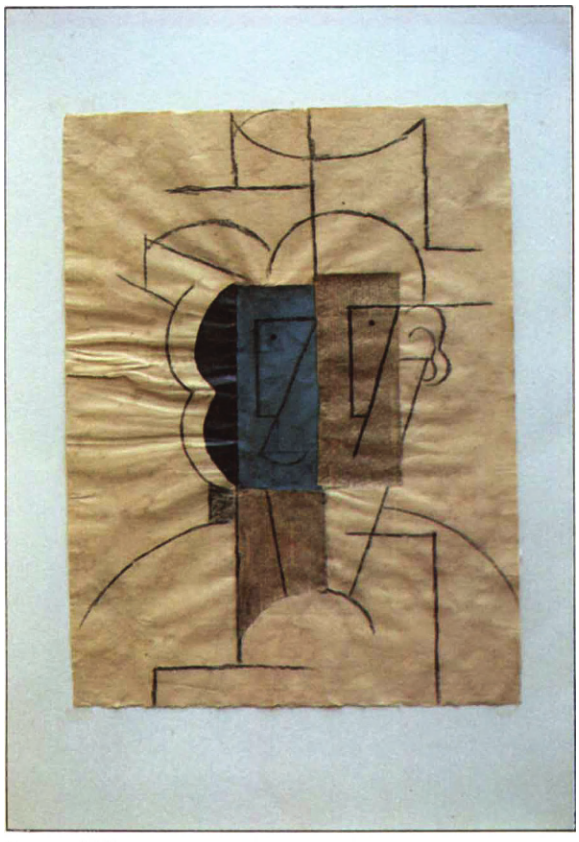

Figure 2.43

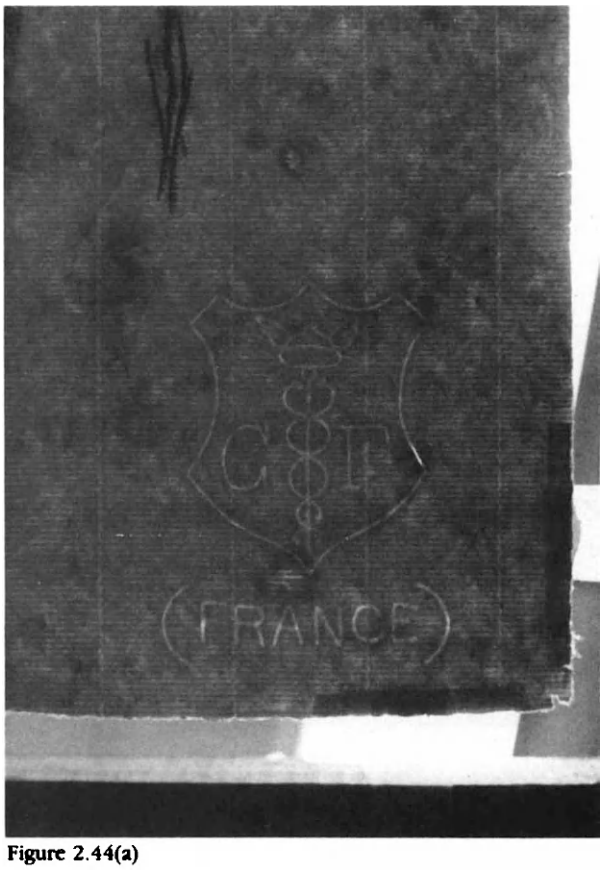

Figure 2.44(a)

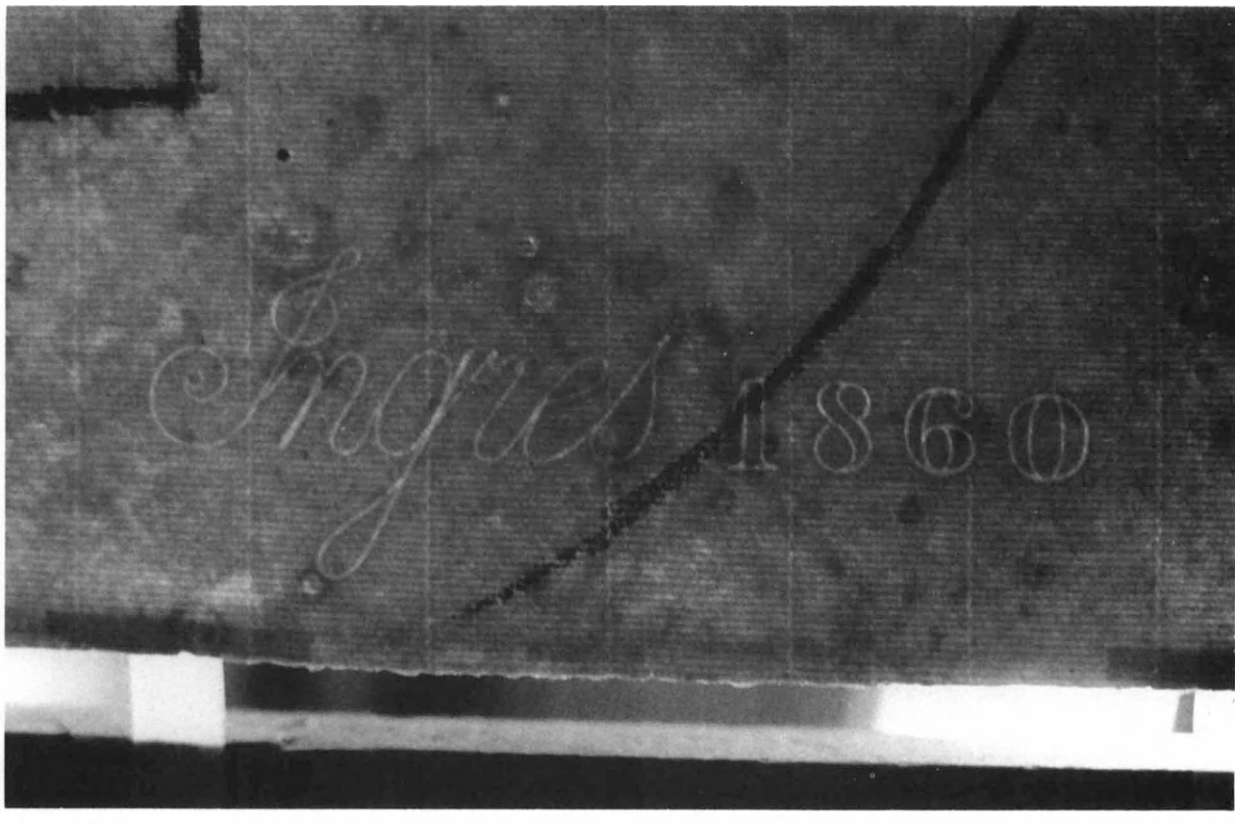

Figure 2.44(b)

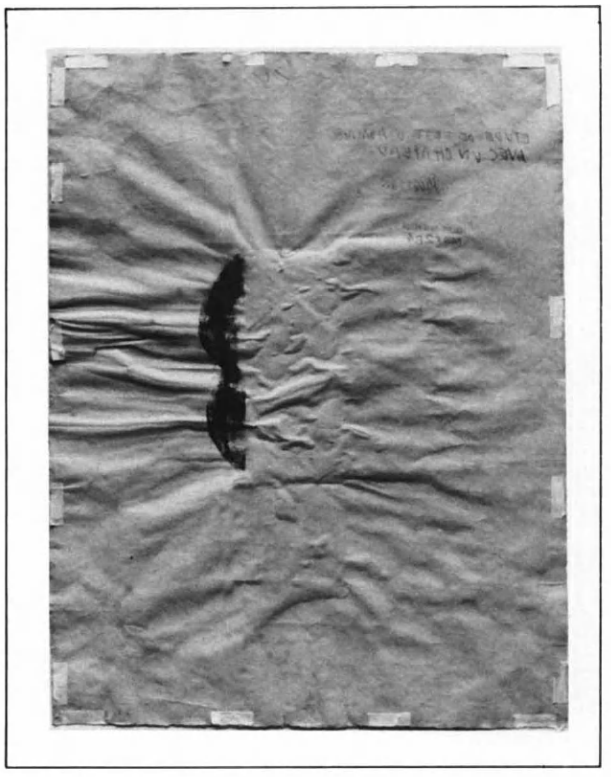

Figure 2.45

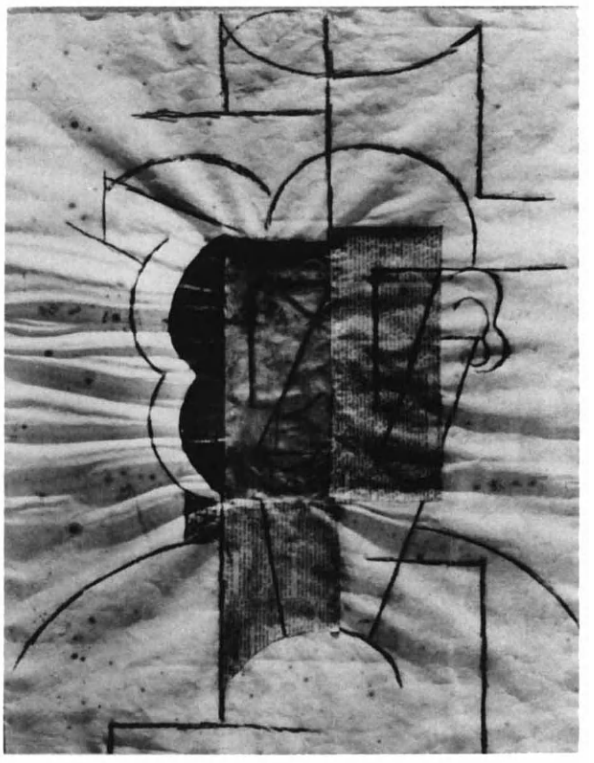

Figure 2.46

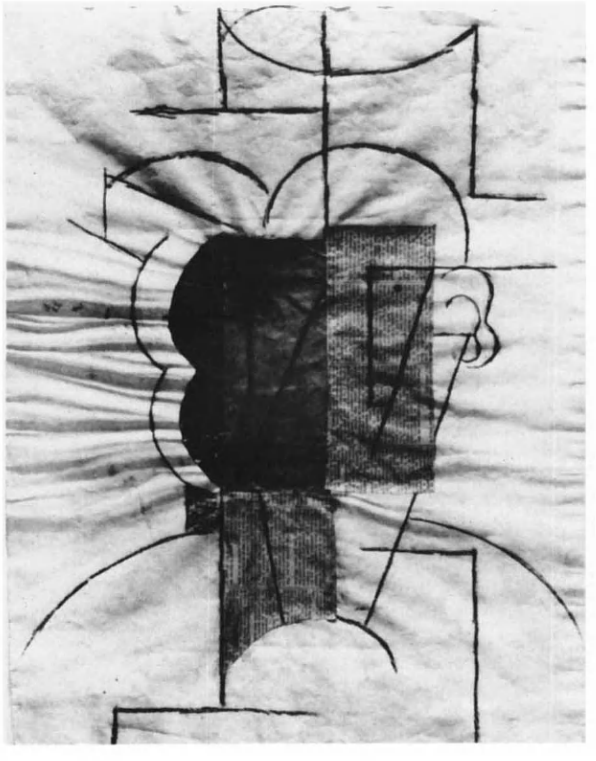

Figure 2.47

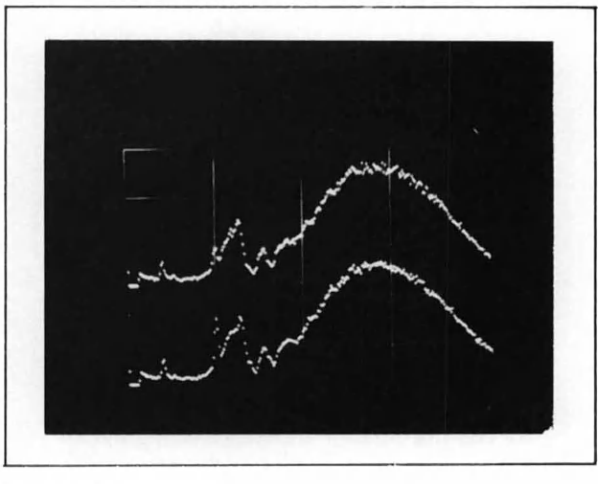

Figure 2.48

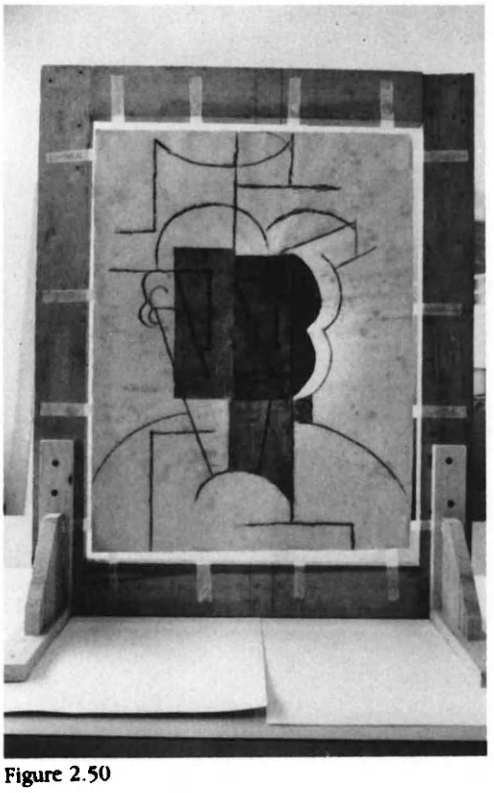

Figure 2.50

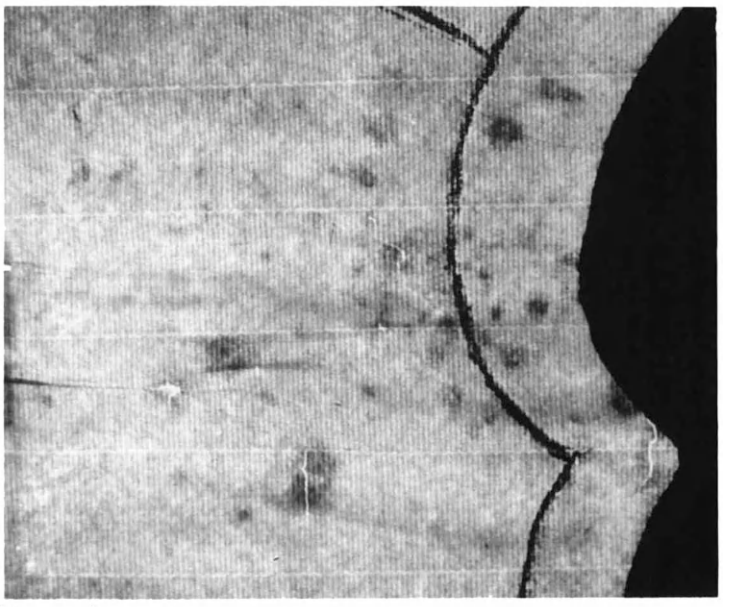

Figure 2.49

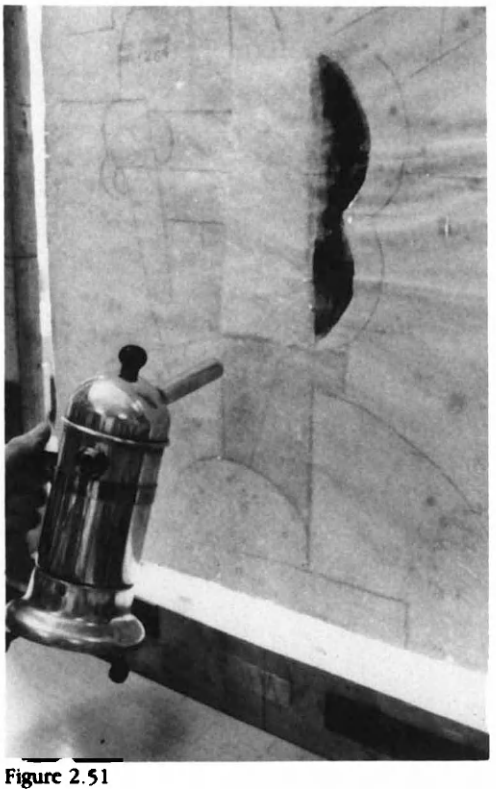

Figure 2.51

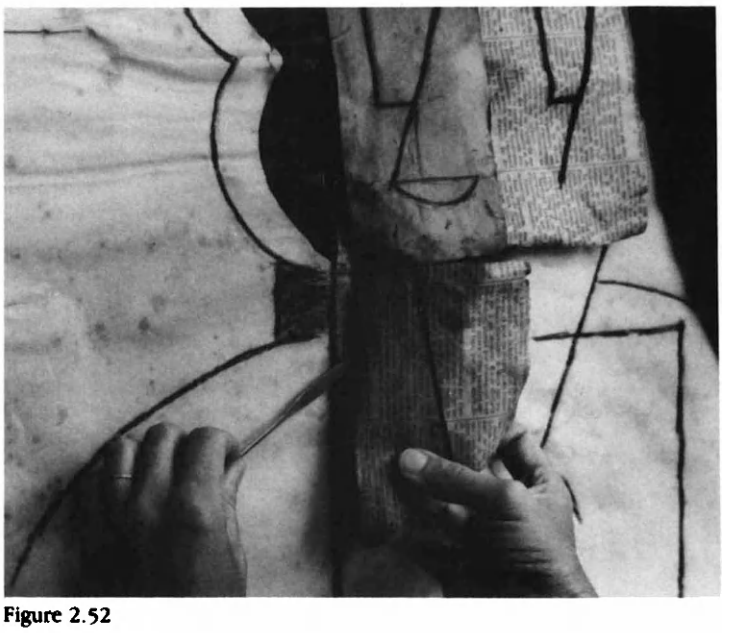

Figure 2.52

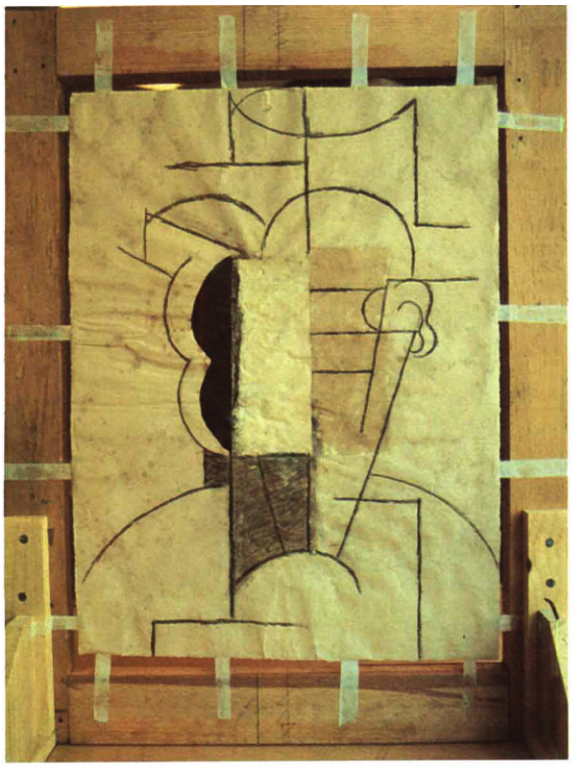

Figure 2.53

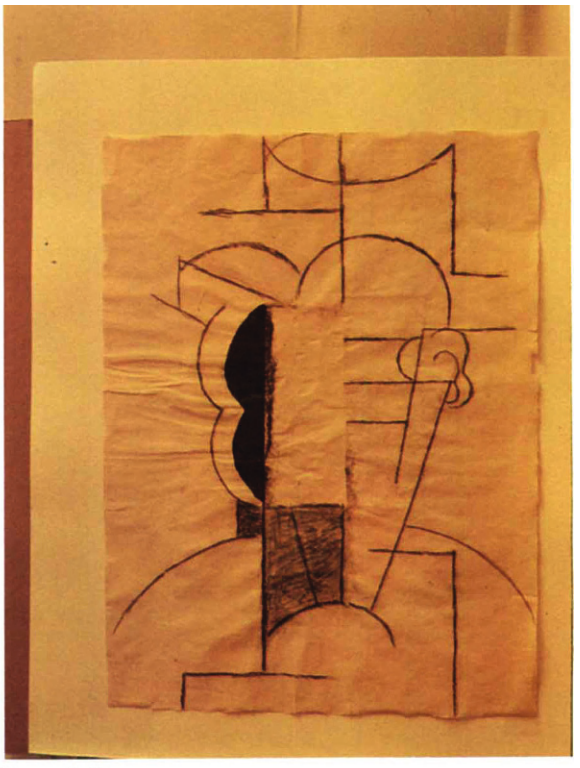

Figure 2.56

Figure 2.54

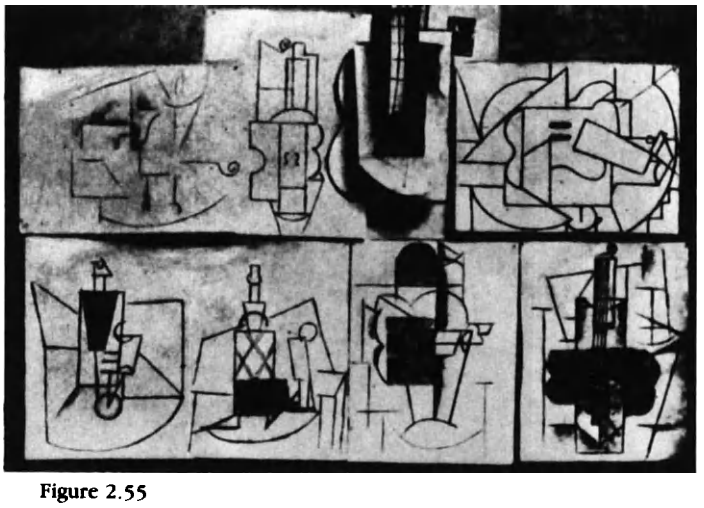

Figure 2.55

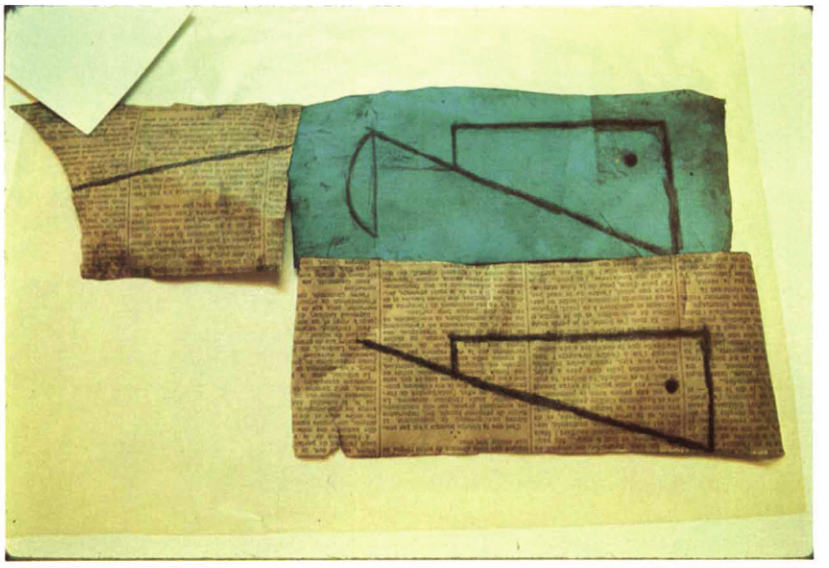

Figure 2.57

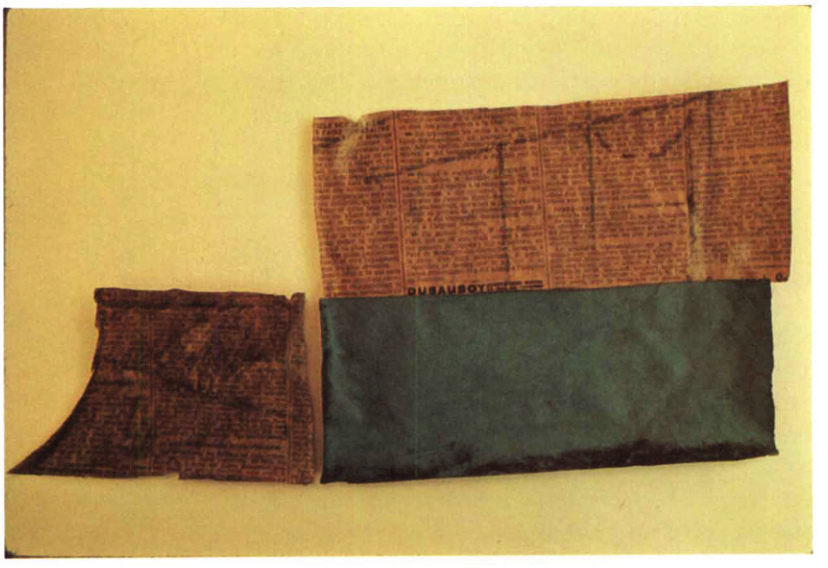

Figure 2.58

Figure 2.59

The blue paper expands when wet but reverts when dry to its original measurement on the picture. The blue paper was lined with a thin *gampi* paper, chosen for its similar coefficient of expansion. The two newspaper pieces were lined with the mulberry paper filled with calcium carbonate. Again, excess moisture was taken out of the lining papers with blotters. Everything was kept as dry as possible and the measurements of all the papers remained the same as they had been when glued on the picture. The pieces were dried on the drying screen, allowing the blue paper to expand and contract freely.

The support paper was still brittle and needed reinforcement. Severe cockles and creases were reduced as much as possible with local application of moisture, and reinforced with thin, water-torn strips of mulberry paper, applied with wheat starch paste. It was hoped to retain the non-planar configuration of the support by moulding the lining to it without overall pressure. However, the support was so weak that it completely flattened on contact with the pasted mulberry lining paper. The areas originally covered by the collage elements retained their exact measurements, however.

The creases had returned somewhat due to the moisture introduced with the lining. Therefore, the lined object was put up on the drying screen, and left just long enough to flatten the creases again, but not long enough to flatten the surface texture of the Ingres paper. The object was taken down while still slightly damp and dried between blotters under a 1/8 in. thick sheet of glass. The papier collé was then reassembled guided by the notations of the pencil marks put under the corners of the pieces when they were originally removed, and with the aid of closeup pre-treatment photographs.

Repasting the entire collage pieces for overall adhesion onto the support sets up the danger of the pieces contracting and cockling, possibly in entirely new configurations. For this reason, this method was avoided. Instead, the collage elements were hinged in their original places on the support with tiny mulberry hinges all around the edges of each piece, adhered with water-thin wheat starch paste. The pieces were small enough to remain flat and thus look glued on, when hinged in this manner. This method was preferred because it is easily reversible *(Figure 2.61)*.

It should be emphasized that such an extensive and potentially risky treatment was undertaken only because the object was, in everyone's opinion, so badly damaged. In the author's opinion, the wit and movement of Cubist papiers collés are too subtle to withstand unnecessary treatment. As Picasso himself said: 'We were trying to express reality with materials which we did not know how to handle but which we appreciated just because we knew that they were not indispensable, that they were neither the best nor the most suitable . . . This move expressed a deep inner need to shatter the bounds of traditional painting, the noble conception of art, and to adapt to art the concrete realities of an industrialized world.'[15]

Notes and References

1. Rubin, William (1972). *Picasso in the Collection of the Museum of Modern Art,* The Museum of Modern Art, New York p.79. 'The three planes of the face in *Man with a Hat* — newsprint, blue and black — are set, unmodelled, in the picture plane. However, they are understood to be in different positions in space, even though they are not seen to be so. The newsprint represents the side of the face catching the light; the blue centre face is in shadow, with the black ink shaping its outer edge'.
2. The reversion of discolourations treated locally with hydrogen peroxide (without stabilizers) has been noted by other conservators in recent times.
3. Private communication, William J. Young. In 'Observations on the foxing of paper', *Int. Biochem. Bull.* **12**, 19, 27-30 (1976), data are presented which 'show that the number of foxed samples is high for low iron concentration, and the number of not foxed samples is high for high iron concentration. Thus low iron concentrations are associated with high occurrence of foxing, which is the reverse of current assumptions.' An article by G. G. Meynell and R. J. Newsam (1978), 'Foxing, a fungal infection of paper', in *Nature* 274, No. 5670, 3 August, 466-468 also points out that lesions (foxing) show no more iron than surrounding paper.
4. Private communication, William J. Young.
5. Manufactured by Glasbläserei Gebr. Möller, Zurich.
6. Daix, Pierre, (1979). *Picasso. The Cubist Years. 1907-1916,* New York Graphic Society, Boston.
7. Gettens, John R. (1952). 'The bleaching of stained and discoloured pictures on paper with sodium chlorite and chlorine dioxide', *Museum,* No. 2, Paris.

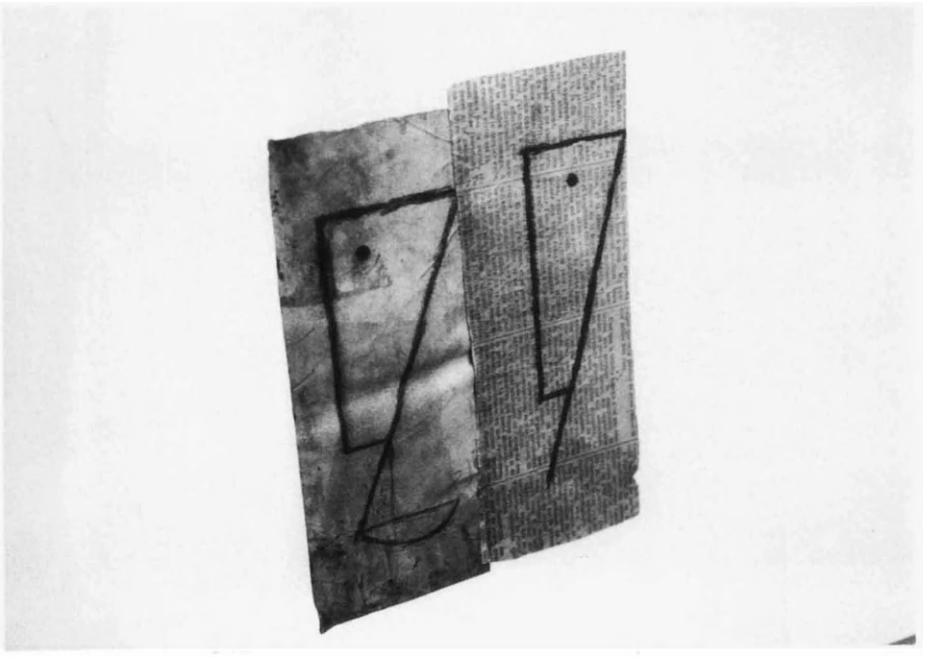

Figure 2.60

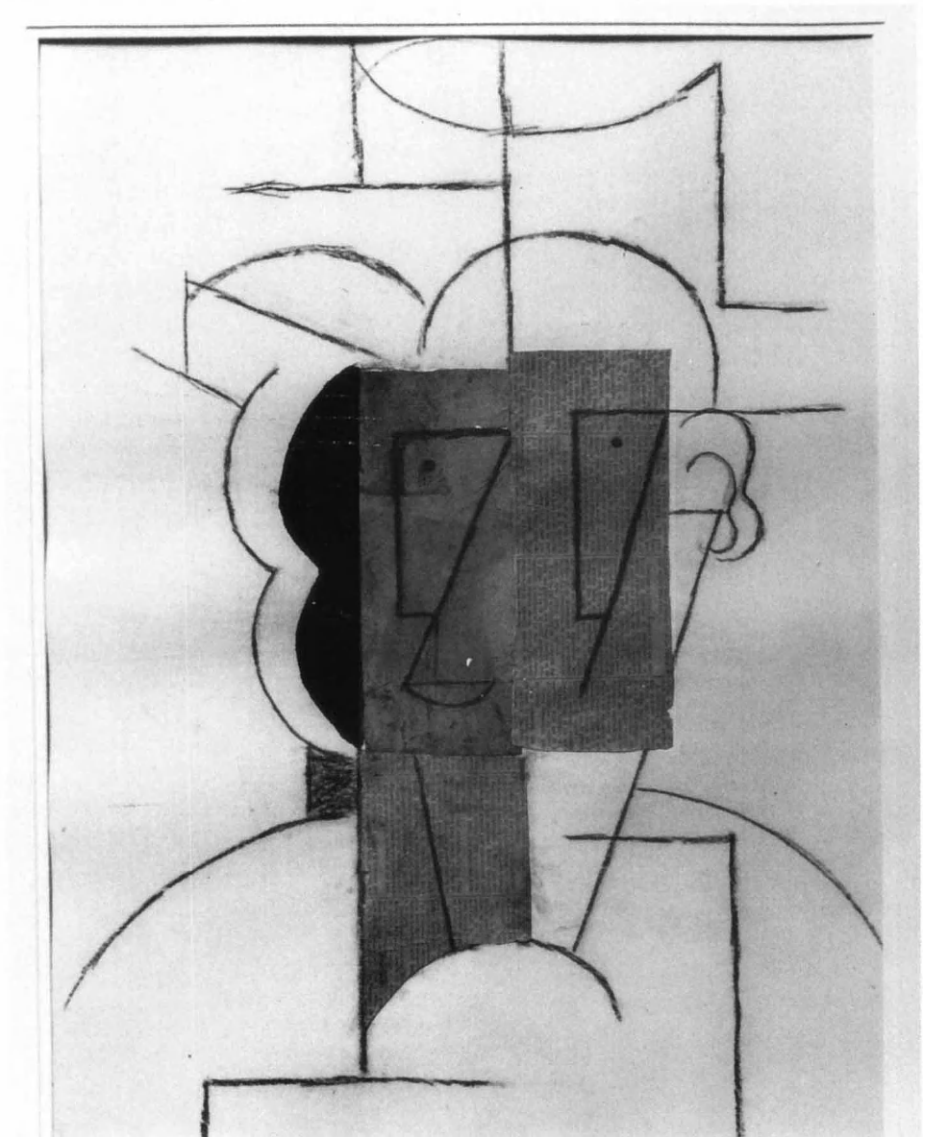

Figure 2.61

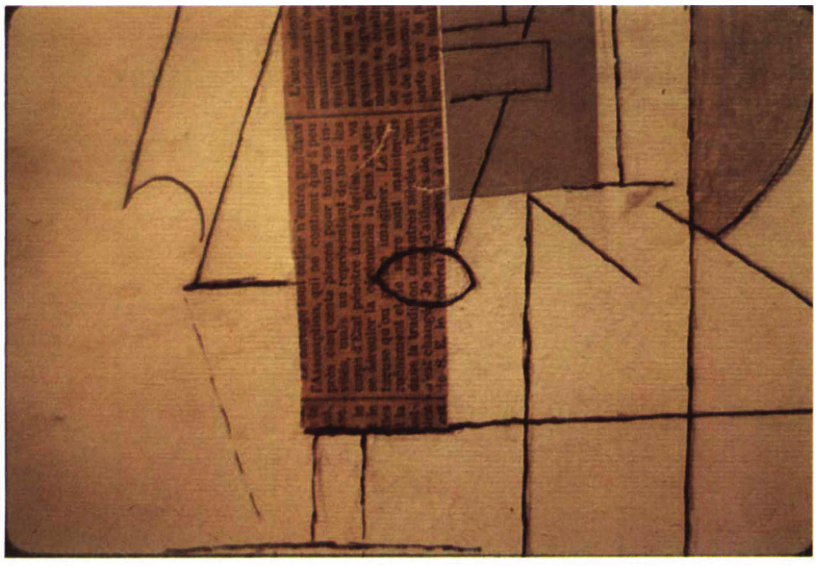

Figure 2.62

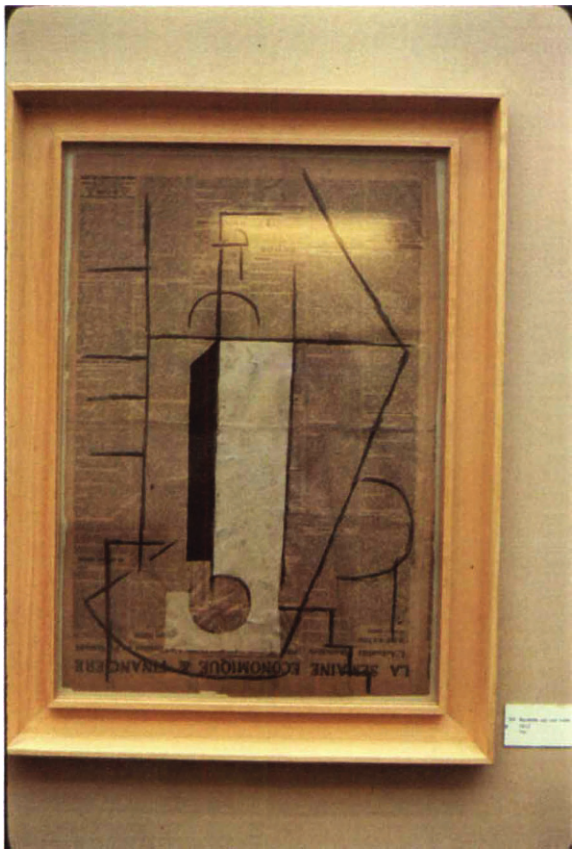

Figure 2.63

8. On adding a few drops of a dilute solution of silver nitrate to a 10 ml sample of the wash water, cloudiness will indicate the presence of chlorides. An amount as low as 1ppm will be faintly visible, according to Carl M. Semczak (1977). 'A comparison of chloride tests', *Studies in Conservation, 22,* 40-41
9. Rubin, (1972), *op. cit.*, p.209.
10. *Bottle and Wineglass,* Paris, autumn-winter, 1912. The Menil Family Collection, Houston.
    Bar-Table with Bottle and Wineglass, Paris, autumn-winter, 1912. Private Collection, Westport, Eire.
    Bar-Table with Bottle and Wineglass. Paris, autumn-winter, 1912. The Metropolitan Museum of Art, New York.
11. Richardson, John (1980). 'Your show of shows', *The New York Review,* 17 July, pp. 16-24.
12. Daix (1979), *op. cit.*, p. 294.
13. Daix (1979), *ibid.*, p.123. 'Picasso could also reverse the internal relationship of a papier collé, using newspaper as a background where the drawing left blank paper, or putting white paper where he had previously had newsprint . . . and the system works equally well'.
14. Daix (1979), *ibid.*
15. Daix (1979), *ibid.*

2.2.5 The conservation of Indian and Moghul miniatures

Phillip Stevens

Many horrific techniques of treatment and repair have and are still being used in the repair of Indian and Moghul miniatures; dry mounting, silking, unnecessary backing, misuse of heat-set tissues and extensive repainting. The use of irreversible surface coatings, soluble nylon, gum arabic, varnishes, etc., completely change the appearance of the miniatures. This paper presents an alternative and rather conservative approach to the treatment of these works of art on paper.

Treatment outline

Tools and equipment

Fume cupboard.
Flat bottomed enamel or stainless steel dishes.
Light table.
× 25 stereoscopic microscope.
Blotting paper (thin, white).
Felt (¼ in. white or beige).
Plate glass (large and small pieces).
Small weights (1-2 lb) (500 g-1k/g).
Fine scalpels [1] and scalpels with disposable blades [2].
Fine needle tweezers (watchmakers' forceps).
Artist sable-hair brushes.
Agate (or similar) burnisher.
Sheets of 0.001 Melinex (Mylar) [3].
Fine chromatographic spray-gun [4].
Gelatine (pure granules).
Methyl cellulose.
Draftclean powder [5].
Drying card (smooth surface card, white, 2 ml thick).

Papers used:
Lens tissue [6].
Japanese mulberry tissue (hand-made *Tengujo*).
Various Indian papers, antique and modern.

Paste: Sodium alginate/arrowroot.
(1) For repair: 10 g arrowroot in 100ml of 1% sodium alginate solution in H_2O.
(2) For backing: 5 g arrowroot in 100ml of 1% sodium alginate solution in H_2O.

Treatment before repair

Dry treatment

Surface dirt is carefully removed by mechanical means. The gentle use of very soft sable-hair brushes with Draftclean powder can be used to reduce ingrained dirt on the paint surface. Ink spots, insect and other debris adhered to the paint surface are removed using a very fine scalpel. This tool can be made from a sharpened sewing needle embedded in an old paint brush handle. Using a × 25 stereo microscope, the foreign matter can slowly be chipped away without damaging the surface of the

paint. All unnecessary backings (i.e. card, linen, cotton, etc.), should be removed dry whenever it is possible without danger of skinning the verso of the miniature leaf.

Solvent treatment

Many Indian and Moghul miniatures have been 'repaired' with, or otherwise damaged by, the use of pressure-sensitive tapes, Sellotape being the most common. Such tapes usually may be removed by application of chloroform working with the miniature in a fume cupboard. Chloroform not only removes the tape, but will remove the residue of adhesive absorbed by the paper and/or paint film which causes discoloured and translucent patches. A range of other solvents including petroleum-based solvents may also be of use in removing types of tape adhesive. No satisfactory solvent has been found for the removal of staining caused by old, dry, oxidized Cow Gum.

Wet treatment

Most monochrome drawings on a single layer of paper can be washed in a bath of water to remove some acidity and staining. This is especially true of those of the Moghul school. Miniatures which are fugitive can be washed by gently floating them on the surface of a dish of water for a long period of time (up to 6 hours). The work being so treated should be lifted from the surface of the water and replaced to its floating position with changes of water, which should be frequent. The paint film may become very soft, but with care this will cause no damage, though the surface must not be touched while wet. The miniature should be dried face up on blotting paper.

A 1:1 mixture of industrial methylated spirit and water is used to remove backing papers, old repairs and any paper adhered to the surface of the paper that cannot be removed dry. This useful mixture (which can be used in differing ratios) is helpful as the alcohol penetrates the pigments and paper quickly taking with it a small amount of water, thus causing them to become less swollen with damp, and consequently less likely to be damaged. The miniature is damped from the back by various means (saturated blotting paper, cottonwool swabs, etc.) after which the unwanted backings are removed carefully from the miniature as it lies face down on plate glass.

Very little chemical bleaching is used, except on monochrome drawings. If the washing methods described above have not removed staining, the miniature may be cleaned with chlorine dioxide. Thorough washing should be carried out after this treatment (at least 6-8 changes of water over a 6-hour period).

Oxidized white and red lead pigments are treated with ethereal peroxide.[7] If it is possible to do so, the miniature is float washed after this treatment.

Methods of repair

All repairs are carried out working on a light table. The simplest form of repair for torn areas, where there is no loss of paper, is carried out with tissues; lens tissue, Japanese mulberry tissue (hand-made *Tengujo*), or very thin pared-down pieces of modern paper. These are adhered to the back of the miniature to secure and support the torn areas. It is important that when using paste for repairs that the film of paste be very thinly applied.

Many Indian miniatures are made up from several layers of paper (two to six), laminated together. When tears occur through these laminates, repairs may be made, using tissues, by folding back these layers of paper until half way through and inserting the prepared piece of tissue at this point *(Figure 2.64)*. The miniature is placed face down on the light table; using a scalpel, the tear is split

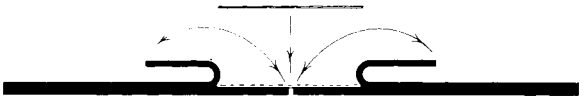

Figure 2.64

horizontally on both sides half way through, then gently folded half back on both sides. The edges of the remaining half should then be pasted together along the tear. A piece of tissue should be selected and pared down to fit the 'channel' between the paper folded back. The 'channel' should then be pasted and the tissue placed in position. The top of the tissue is then pasted, also the edges of the paper folded back, after which they are returned to their original position. The repair is then gently burnished through blotting paper; and finally pressed between blotting paper or felt using plate glass and a 1 lb (500 g) weight.

Where areas of lamination are weak and separating from each other, paste may be applied between each layer and pressed dry. A tissue support is not always needed, but may be inserted between the laminated sections, if necessary.

If a miniature has many tears and weak areas it is possible to split the layers of lamination when dry.

All tears and damages are then pasted into their correct places on both sheets of paper and the miniature is then reassembled with strong Japanese tissue (hand-made *Tengujo*) in the centre. 5% arrowroot paste in sodium alginate solution should be used for this operation. When reassembling the laminated pieces, great care is needed to make sure the miniature is not made too damp so as not to cause damage to the pigment layer.

Miniatures in a weak and fragmented condition made up from many layers of paper can be completely dismantled, and reassembled retaining only the original back paper with the miniature's support and bringing the centre laminates up to the same original thickness with either antique or modern Indian papers. This operation should only be carried out when these centre laminates are beyond preservation, i.e. completely rotten or embrittled.

Repair of missing areas

As well as conforming to conservation criteria in the selection and use of materials, it is important to obtain as visually perfect a repair as possible and in seeking this end Indian paper contemporary with the miniature is used. Great care is taken in selecting a suitable paper, taking into account weight, thickness, colour and surface texture.

First the laminated papers of the miniature are split in the damaged area to allow Japanese tissue to be pasted within the centre of these laminations in a similar manner to the tear repairs *(Figures 2.65* and *2.66).* After being lightly burnished through blotting paper the miniature, with the tissue in place, is pressed between blotting paper with glass and weight to dry.

Figure 2.65

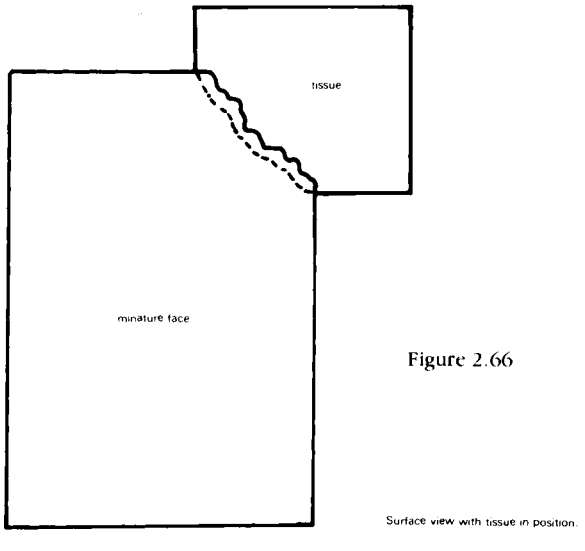

Figure 2.66

When completely dry the miniature is then placed face down on a light table and a small piece of Melinex is placed over the area to be repaired. The selected Indian paper is then placed on top of the Melinex and with a scalpel the paper is then pared out to meet the edge of the miniature exactly. This paper is then put aside, pared edge face up. The next step is identical, but in reverse. The miniature is turned over and, again using Melinex as a transparent barrier guide, the repair paper is pared out. The first pared repair paper is then pasted on the pared surface then placed exactly in position on the Japanese tissue just touching the miniature. The miniature is then turned over and the process is repeated pasting the pared surface of the repair on the back of the miniature. When this is completed, the Melinex is placed on the back of the miniature, and with the front face down on the glass of the light table, it is gently burnished.

Finally it is pressed locally face down on the light table covered with a piece of felt over the repair, a small piece of glass and a 1 lb weight giving enough pressure. This should then be left in place for at least 10 minutes.

The above method describes the repair of a miniature comprised of two laminations, the pigment support and the back. If, as in many cases, the miniature is made up from many layers of paper the same number of repairs have to be made so as to bring the repaired areas up to exactly the same thickness as the original laminations. It is most important that all pared surfaces face towards the centre. The result gives a very neat and smooth join where the repairs meet the undamaged areas.

Insect holes are repaired with long fibres separated from Indian paper and mixed with very dilute paste. This is then applied when the pulp is almost dry. Very large worm or insect holes are repaired in the same way as missing areas.

Finishing

It is important to be accurate when trimming away surplus repair paper and tissues. Small pieces of visible repair tissue spoil a fine repair. When trimming with a scalpel, if you have replaced a corner, make it the same shape as the other three corners! Very gently burnish all the scalpel cut edges to remove the sharp edge.

Pressing

Usually enough pressing is automatically carried out as the miniature is being repaired. If more pressing is needed a chromatographic spray may be used to slightly damp the miniature from the back. After this, the miniature is then placed face down on a drying card and covered with felt. Felt is used as it allows for variations in thickness of laminated papers. A sheet of plate glass is placed over the felt and weighted down. If the miniature has a very heavy impasto, it should be dried face up in contact with the felt.

Sizing

When it is necessary to size the repaired miniature, gelatine or methyl cellulose is used. A 10% solution of pure gelatine should be applied to repaired monochrome drawings comprised of a single paper layer, on both sides commencing with the verso. Excess should be blotted off. Methyl cellulose may be applied locally to repairs to assist with the even toning of the repairs to bring them up to the same tone as the damaged miniature. A 2% solution of methyl cellulose in water should be applied, lightly blotted off then dried under pressure between fresh blotters before commencing toning.

Facsimile

Many fine Indian and Moghul miniatures and manuscript pages have been completely ruined by extensive re-painting. Facsimile techniques and retouching should be carried out only after a great deal of thought and discussion.

Retouching should be limited to the front surface of the repair paper only. The repair paper may be toned in to blend with the colour of the original miniature, missing borders may also be touched in so that the repaired areas do not seem obtrusive. The final result must leave the repaired miniature in a condition that is visually undisturbed by the repairs, and aesthetically pleasing to view.

Notes and References

1. Small tenotomy knives (GR 310-01-G), obtainable from Downs Surgical Ltd., 32 New Cavendish Street, London W1, England.
2. Swann-Morton carbon steel VPI protected surgical blades obtainable from art suppliers and chemists, also from Swann-Morton Ltd., Sheffield S6 2BJ, England.
3. Melinex, a transparent film of poly (ethylene terephthalate) manufactured by ICI, England.
4. Fine chromatographic spray-gun obtainable from Baird & Tatlock, PO Box 1, Romford RM1 1HA, Essex, England.
5. Draftclean powder obtainable from Archival Aids, Ademco Ltd., Coronation Road, Cressex Estate, High Wycombe, Bucks, HP12 3QU, England.
6. L2 tissue obtainable from Barcham Green & Co. Ltd., Hayle Mill, Maidstone, Kent, ME15 6XQ, England.
7. Plenderleith, H. J., and Werner, A. E. A., (1971). *The Conservation of Antiquities and Works of Art,* London, p. 87.

2.2.6 A conservation method for Islamic illuminated manuscript leaves

Frederick Marsh and *Julian Clare*

A method of dry-repair is described designed to reinforce weakened or detached frames and edges of Islamic illuminated book leaves. The technique aims to give transparency, stability, flexibility and strength without undue bulking. Also described is a process for tinting, dyeing and coating with a heat-set adhesive various repair papers to blend with the original manuscript leaves.

Introduction

The style of repair discussed here was formulated to solve a problem characteristic of certain Islamic illuminated manuscript leaves where rectangular frames have been drawn around the illuminated areas with a verdigris ink or an unstable copper ink simulating gold which produces acidic degradation products which attack the paper of the leaves. The leaves break up along the acid-attacked delineated frames and the illuminated areas eventually fall out.

In the past a commonly used method by restorers to hold such damaged leaves together was to paste a thin French silk tabby fabric over the entire page. Among the many disadvantages of this method was the two- or threefold increase in leaf thickness and the imprinting of the weave of the silk on the pigment layer revealed when the silk is removed at a later date (the durability of such silk used in these circumstances is itself debatable). The edges of the silk fray, making the repaired leaves unsatisfactory to re-bind.

The India Office Library and Records Conservation Department have been developing a form of repair which aims to give transparency, stability, flexibility and strength without bulking. Because the original paper of any manuscript varies from volume to volume and, indeed, may vary within any one volume, there can be no hard and fast rules as to the kind of repair paper used. The choice must inevitably lie with the individual conservator, but the basic principles will remain the same as those for the manuscript which is used here to illustrate this technique.

Preparation of repair materials

After examination of characteristic Islamic manuscript leaves, the majority of which are formed from flax fibre, and observing that many of the pigments used for the illuminations are unstable in an acidic environment, we decided to use Japanese papers for repair, of neutral or slightly alkaline pH, because they are the only available papers light enough yet strong enough to achieve the desired results. However, the Japanese papers obtainable in Britain are basically white in colour and to obtain an aesthetically pleasing repair we required a toned paper. We therefore decided to investigate the possibility of a dyeing technique for Japanese papers which is stable and light fast. We use the term *aesthetically pleasing* because in our conservation

section we do not repaint missing areas of miniatures but we do take conservation, by using visually sympathetic materials, to a stage where repainting would be possible.

We selected three repair papers; one for the broken frames and two for the page edges. The paper chosen for the frames was *gampi* tissue (approx. 0.04 mm thick)[2] which, when coated.with adhesive, gave both the fineness and the transparency which we needed. For the edges *hodomura* paper[3] (approx. 0.11 mm thick) and Barcham Green's L2 tissue[4] (approx. 0.05 mm thick) were selected, the latter because it is a fine paper of pure cotton fibre. These two papers can be used together to make up the total equivalent thickness of the leaf to be repaired. There are a number of Japanese papers which could be used for this work but very few European ones.

After assembling sufficient L2 tissue and *hodomura* paper to complete the repair of the volume, they are dyed to a shade which would make the repair visually sympathetic with that of the original manuscript paper (see colour samples with formulas for use in this work), with consistent colouring throughout. The dye used is Dylon cold water dye,[5] an organic commercially produced dye. The dye is mixed to the manufacturer's instructions and diluted to shade. The fading and ageing tests which we were able to carry out indicated that the colours are durable and have no discernible deteriorating effect upon the paper or pigments on which we have used them.[6]

We adopted the following method of dyeing Japanese paper in bulk: the dyes made up according to the manufacturer's instructions are added to 20 gallons of cold water in a large sink. It is necessary to add a mordant to fix the dye. This is also sold by Dylon International Ltd. under the tradename Dyefix. Analysis indicates that it is no more than sodium carbonate. A papermaker's felt is then laid on the surface of the dye, then five to ten sheets of repair paper depending on their weight and rate of absorption, another felt, more paper, and so on until the required amount is immersed in the dye bath. If papermaker's felts are not available, a good wet-strength paper like Multisorb[7] can be used instead. We also found that felts could be dispensed with if dyeing baths are only a little larger than sheet size. As the Japanese papers will not adhere to one another when wet and will easily separate for drying interleaving felts are not absolutely necessary for them although they are imperative for the European L2 tissue. We found that a maximum of five sheets of *hodomura* paper could be successfully dyed between each felt, but up to ten sheets of a lighter weight paper such as L2 tissue or *gampi* tissue. The paper is left in the dye for one hour. After dyeing the block of felts and paper (or paper alone for the Japanese material) is removed from the bath and allowed to drain. After draining the block is separated and each batch of paper is hand pressed between heavy-weight blotting paper to remove excess moisture. Each batch of paper is then interleaved with absorbent paper and left to dry under pressure. The absorbent paper is changed periodically.

When completely dry the *hodomura* paper and the *gampi* tissue are coated with a heat transfer adhesive (i.e. an adhesive which is supplied as a coating to a silicone backing paper from which it can be transferred to another sheet of paper by the use of heat in a photographic dry mounting press or by ironing with a commercial iron), Lamatec,[8] produced by Ademco Ltd. (30 seconds at 60°C between silicone release papers or PTFE cloth). This adhesive was chosen because it is a non-externally plasticized poly(vinyl acetate) which reverses quickly in 1,1,1-trichloroethane (CCl_3CH_3) or chloroform ($CHCl_3$). Tests undertaken at Her Majesty's Stationery Office laboratory[9] indicate that 'Infra red did not produce evidence of adhesive breakdown or crosslinking' and that 'Over a 160 day period of ageing at 60°C (approximately equivalent to 175 years at 20°C) no evidence was discovered to suspect that Lamatec adhesive contributes to the paper fibre degradation.'

The *gampi* tissue is coated with Texicryl 13-002[10] which is a milk-white emulsion, having a dispersion of 55% solids in water, of acrylic ester copolymer. The monomers in the co polymer system are ethyl acrylate, methylmethacrylate and methacrylic acid. Primal AC34[11] can also be used. Both are acrylic resins and both are diluted with 65% of magnesium bicarbonate ($Mg(HCO_3)_2$) solution. The prepared acrylic adhesive is brushed onto a sheet of clean dry glass with a 37 mm soft-haired brush, using single strokes which overlap the preceding stroke until a continuous even coating of adhesive is obtained. The *gampi* tissue is then laid down slowly onto the adhesive, taking care not to trap any air, and any surplus adhesive is removed from around the edges before leaving the tissue to dry. The dry tissue is slightly moistened with a sponge so that it can be peeled away from the glass. Another method of coating used is to float the tissue onto the surface of a tray of adhesive. The coated tissue is then laid adhesive side down on glass to dry. The advantage of this method is that the prepared sheets dry flatter. Each sheet is then interleaved with silicone paper for storage until required. We use *gampi* paper for this coating technique because it is a paper with a polished finish

and, if the adhesive has been carefully applied, it will not penetrate through the paper to the other side, thus eliminating the possibility of secondary blocking at a later stage. These adhesives are reversible in the same way as for Lamatec. *Gampi* tissue prepared in this way is transparent.

The HMSO report on the archival permanence of Texicryl laminates indicates that magnesium bicarbonate aids in the reduction of blocking of laminated papers. The HMSO laboratory prepared their adhesive by thoroughly mixing 40 parts of original Texicryl emulsion with 60 parts of a magnesium bicarbonate solution prepared by dissolving 100 g of magnesium carbonate in 15 litres of water and bubbling carbon dioxide gas through it for one hour.[12] This reduction in blocking is confirmed by tests carried out in our own department on 2*gmpi* papers coated with Texicryl 13-002.

Repair techniques

The leaves to be repaired undergo the normal preparatory work; examination, photography and documentation. Any old repairs are removed before new repairs are applied. In the case of tenacious early repairs, moisture is introduced to their adhesive stratum by applying extremely viscous carboxymethylcellulose paste on top of the repairs which has the advantage of confining the moisture required to a selected area, while at the same time softening the old adhesive sufficiently to allow removal.

Two pigments which are frequently encountered in Islamic manuscript illumination are white lead (basic lead carbonate) and red lead.[13] Both pigments are likely to have been affected by sulphuretted hydrogen gas present in industrial atmospheres which causes blackening (lead sulphide) of the pigmented areas disfiguring the miniature painting. A treatment of hydrogen peroxide (H_2O_2) and diethyl ether ($(C_2H_5)_2O$) will often restore the pigments to their original appearance. A method used at the India Office Conservation Department is to mix equal parts of 30 volume hydrogen peroxide and ether together in a separating funnel. These liquids are immiscible — the aqueous layer containing any impurities remains at the bottom. It is then possible to drain away the impure layer leaving ether containing sufficient hydrogen peroxide for bleaching purposes. The ethereal mixture is then applied directly to the pigment with a soft-haired brush.[14]

Great care must be taken to test the pigments treated in this way as it is possible for certain pigments to evacuate through the paper. Indian yellow, quite often mixed with blue to form green, is an example. If testing suggests the possibility of such damage occurring, another method may be used: The ethereal mixture is prepared in the same way. A fine wire mesh is suspended over the pigmented area to be treated, but not in contact with it. A piece of cotton wool is soaked with the mixture and laid onto the mesh. Ether, being a heavy gas, will fall onto the affected area, producing the same effect as direct application but without danger to suspect pigments. Although slow, this method is much safer.

Where necessary, we consolidate pigments by brushing or localized spraying with 1.5% soluble nylon (N-methoxymethyl nylon (Calaton)) in methanol (CH_3OH) with 0.75% barium hydroxide ($Ba(OH)_2 8H_2O$) added as a deacidification agent. It is seldom necessary to use soluble nylon but, if so, it is essential that both the paper and the solution be of alkaline pH, otherwise there is a serious danger of the soluble nylon cross-linking, thus reducing the possibility of reversing the fixative at a future date.[15] It must be emphasized that this treatment should only be used as a last resort and not, as some conservators do, as a general fixative. When fixing with soluble nylon is not necessary, each page may be sprayed with barium hydroxide in methanol as a deacidifying agent for the acidic pigments.

To begin the paper repair the leaf is placed between heavy-gauge Melinex, a clear polyester film, to protect it from handling and from damage by the needle or stylus used in this technique. A single sheet of undyed *gampi* heat-set tissue is then placed over the Melinex and, working over a light box, the frame is carefully traced with a needle, weakening the tissue but not cutting it, so as to leave about 3 mm of tissue on either side of the frame *(Figures 2.67* and *2.69)*. The tissue can then be carefully torn along the weakened lines *(Figure 2.68)*. When the operation is completed all around the frame the leaf is turned over for a repetition of the process on the reverse. The shaped *gampi* tissue is then carefully placed into position over the frame with the aid of the light box and lightly ironed down with a heated spatula, using a piece of silicon paper as a protective barrier *(Figure 2.70)*. A scalpel is used to cut away the unwanted overlap of repair tissue *(Figure 2.71)*.

Where the leaf has small holes caused by insect damage, etc., these are then filled in with dyed paper fibre prepared by placing small torn pieces of Barcham Green's L2 tissue into a food blender with distilled water. This is then beaten until the fibres separate. The water is drained off and a small amount of stock solution of the appropriate Dylon dye (with mordant) is added to give the required

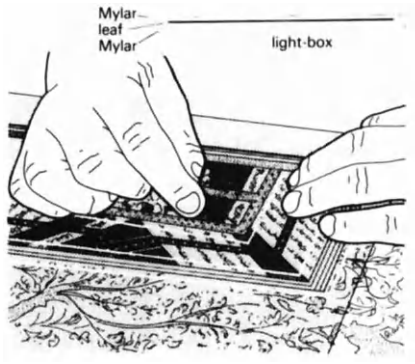

Figure 2.67. Using a heavy Melinex barrier to protect the leaf (lit from beneath by a light box), a needle is used to score the reinforcing *gampi* tissue.

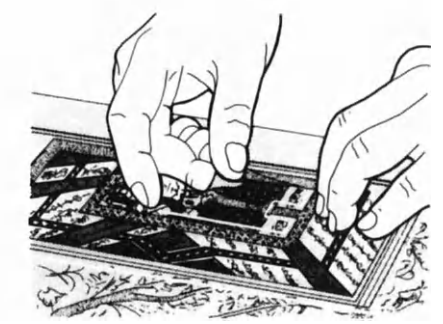

Figure 2.6.8. Removing the surface *gampi* tissue.

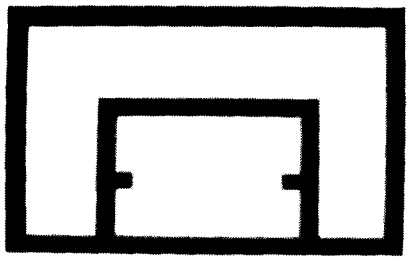

Figure 2.69. A diagram illustrating the pattern of the remaining repair tissue. The lighter areas are to be trimmed away in a later operation. The cross section indicates the way in which the leaf is protected temporarily with two Melinex sheets, the top line representing the repair tissue.

Figure 2.70. The leaf is laid onto a silicon paper protected board. The repair is attached loosely using a heated spatula through a silicon paper barrier.

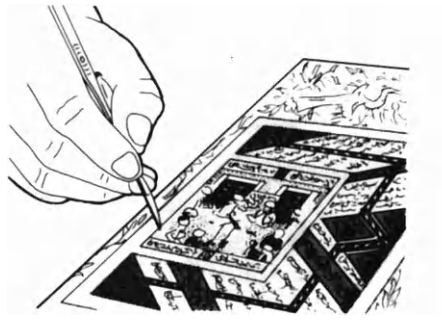

Figure 2.71. A scalpel being used to cut away the unwanted overlap of repair tissue (indicated by the lightly shaded area in Figure 2.69.

Figure 2.72. Leaf placed onto a clean, dry sheet of glass. Working over a light-box the lacunae are filled with pulped L2-tissue which has been dyed and mixed with Texicryl as a binding agent. The fibre is built up in the lacunae using watchmaker's foreceps. The reverse end of the foreceps is used to partially consolidate the pulp by applying pressure.

tone plus a little Texicryl adhesive as a binder. The leaf is laid on a clean dry sheet of glass and the toned pulp is manipulated into the holes with a small pair of tweezers *(Figure 2.72)*. It is advisable to overfill the holes to allow for shrinking. To consolidate the infill, a heated spatula is applied, again using silicon paper as a protective barrier *(Figure 2.73)*. If the infill is still above the level of the leaf surface when dry, a scalpel is used to pare it back to the thickness of the leaf. Magnesium carbonate light $(3MgCO_3Mg(OH)_23H_2O)$ is then brushed over all the repaired areas, the leaf is placed between silicon paper and all the repairs are consolidated by using the heated spatula, but this time with a light pressure. Magnesium carbonate at this stage is not intended as a deacidification agent but its very fine powder will absorb any excess adhesive which was added to the pulp as a binding medium when infilling holes. The magnesium carbonate thus forms a protective layer against blocking.

The frame repair is now completed and the borders of the manuscripts should show clearly and unobscured.

In many cases only the frames need repair, but the manuscript used to demonstrate the technique in this paper also had weak and damaged edges to the leaves. Such damage is reinforced in the following way. L2 tissue dyed and then coated with heat transfer Lamatec is, once again allowing a 3 mm overlap onto the damaged edges of the leaf, marked out, torn into shape, and applied with a heated spatula as for the frames *but to one side of the leaf only,* preferably to the side which has no painted miniature *(Figures 2.74 to 2.76).*

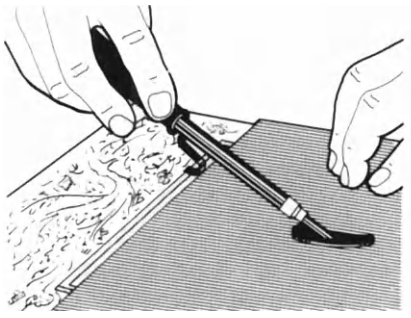

Figure 2.73. The leaf is placed onto a silicone paper protected board with a silicone paper overlay. Heat is applied with a spatula to consolidate the fibre infill.

Figure 2.74. Using the Melinex barrier as in Figure 2.67, coated L2-tissue is scored round the edges of the leaf undergoing repair with a needle, leaving an overlap of 3-4 mm (see diagram Figure 2.75).

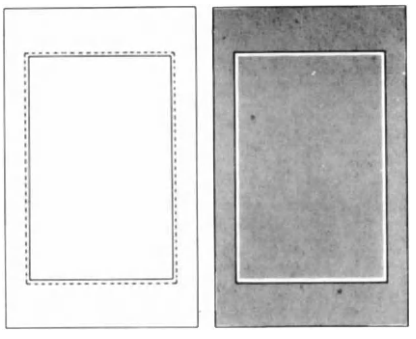

Figure 2.75. Figure 2.78.

Figure 2.75. Diagram of area needled out as described in Figure 2.74.

Figure 2.78. Diagram showing line scored by needle as described in Figure 2.77.

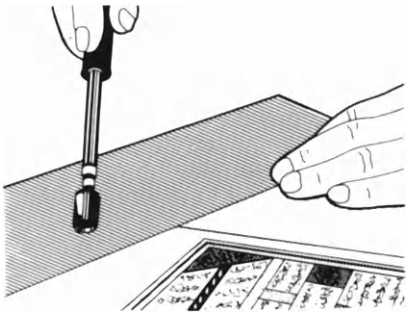

Figure 2.76. Using the same protective barrier as the border repair Figure 2.70, L2-tissue is lightly tacked into place with the heated spatula.

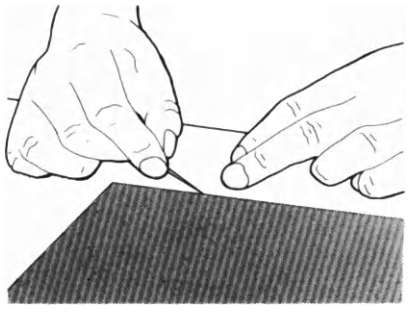

Figure 2.77. Using a protective Melinex barrier (as in Figure 2.67) *hodomura* paper is marked with a needle leaving 1-2 mm overlap (indicated by the light area in Figure 2.78).

Figure 2.79. Working on a clean, dry white blotting paper over a lightbox, the L2-tissue is cut back with a scalpel until only 1-2 mm remain on the page. The page is turned over and the *hodomura* paper is cut back until the repair appears to be an extension of the paper of the artefact itself. Finally all repairs are consolidated with a commercial, large-headed spatula.

Hodomura paper, dyed and coated, is used as an infill paper, marked out with a needle around the edge of the leaf, but leaving only about 1 mm overlap, torn into shape and then ironed into position (always over a light box) with a heated spatula. Finally a scalpel is used to pare back the overlap of the fill-in until blended into the edge of the original paper *(Figures 2.77 to 2.79).*

When the edges are completed the repair has the appearance of being an extension to the page rather than an overlapping repair. At the spine edge of each leaf a 50 mm extension may be left as part of the leaf. This can then become a functional part of the rebinding, allowing each leaf to swing on new and more flexible paper and thus minimizing stress on the repaired border adjacent to the spine which, even after repair, is still the weakest part of the leaf. When a manuscript has to be rebound, all pages with illumination are interleaved with acid-free tissue paper before resewing.

Although, above, we have expressed caution regarding the use of certain chemicals, it would only be correct to elaborate a little further on these warnings. It would be unwise to consider these techniques suitable for all types of illuminated material. Further research still has to be done into the effects of the dyes and on their fading properties. One must remember that colours vary in their constituent pigments/dyes and that the binding media vary. In the case of oriental pigments and dyes insufficient work has been carried out into their individual properties and chemical interactions with other materials including binding media let alone with the conservation materials in contemporary use. Very careful testing must be carried out to ensure that heat, even at moderate levels, does not cause colour change or chemical decomposition. The solvents which might potentially be used to reverse heat-set adhesives might themselves cause damage to painted or text areas. Gamboge, for example, is highly fugitive in water and non-aqueous solvents such as acetone. Though the correct grades of PVA do have a limited use in conservation, it is very vulnerable to thymol, which dissolves the resin causing ugly greasy marks. The flow of resin as it plasticizes away from the repair paper weakens any strengthening effect. Artifacts repaired with PVA adhesive should *never* be fumigated with thymol either in a chamber or by the use of impregnated interleaving paper. It should be considered essential that, where the methods described above have been used, a record of the substances used be kept with the repaired volumes for the reference of future conservators.

Notes and References

This article appears in *The Paper Conservator*, 4, 3-9 (1979).

1. For an excellent commentary on and translation of an eleventh century Islamic text containing recipes for inks (including copper inks and green inks from verdigris), dyes, etc., see: Levey, M., (1962). *'Medieval Arabic bookmaking and its relation to early chemistry and pharmacology'*, *American Philosophical Society*, New Series, **52**, Part 4.
2. *Gampi* tissue (dimensions 450 mm x 610 mm) is available from Falkiner Fine Papers Ltd., 117 Long Acre, London WC2E 9PA.
3. *Hodomura* heavy cream wove is used. It is available from Falkiner Fine Papers (see Ref. 2). In the text paper substance is given in thickness in mm and not by weight in gm^2 because the sheets vary in thickness within each batch, and for the technique described above the paper thickness (caliper) is of prime importance.
4. Manufactured by Barcham Green & Co. Ltd., Hayle Mill, Maidstone ME15 6XQ, Kent.
5. Dylon cold water dyes are manufactured by Dylon International Ltd. Worsley Bridge, London SE26. The authors found that dyes with the trade names 'Summer Sun' and 'Koala Brown' produced tones most sympathetic to the Islamic papers being conserved. When using the dye, it is advisable to wear rubber gloves and protective clothing.
6. Tests carried out to determine the fading and ageing characteristics of Dylon dyes in conjunction with *gampi/hodomura/*L2 tissue: Samples of these papers were dyed with Dylon cold water dyes and dyed and toned with other media commonly used for colouring repair papers (tea, coffee, aniline brown and watercolour tints). Ten samples of each dye/paper combination and of undyed *gampi/hodomura/*L2 tissue cut to a standard 100 cm^2 (10 cm x 10 cm) were exposed to ultra-violet radiation (7.5μW uv as measured Littlenox uv monitor Type 678) from a standard uv library examination lamp (manufactured by P. V. Allen & Co., 253 Liverpool Road, London N1) with the safety filter removed (the tests were carried out within a shielded safety case) for 168 hours continuously. These exposed samples were then compared with unexposed control samples.

While the exposed samples coloured with the commonly used colouring agents faded quite considerably, the Dylon dyed papers showed no visible signs of fading. Exposed samples were also placed in an accelerated ageing oven for 72 hours at 105°C in a standard fan-blown ageing oven (which would mean at virtually nil RH) and then compared with 'unaged' uv exposed samples, with dyed samples not exposed to either uv or accelerated ageing and with undyed samples as to pH (surface measurement) and folding endurance (samples conditioned and tested at 55 RH and 18°C). The Dylon dyed samples showed a no faster deterioration rate than the undyed control samples and the Dylon dyed papers were still markedly superior in their retention of their tones.

These tests were also carried out for paper samples coated with Texicryl 13-002 laminate adhesive. It is possible that the test results may be altered with other adhesives. Further tests are planned to ascertain fading properties at other illumination levels and in other simulated conditions. Fading is influenced by the chemical and physical nature of the fibre; by the temperature and humidity of the environment; sulphur dioxide and ozone can cause fading and fading can occur in the absence of light, e.g. under the influence of nitrogen oxides. See: Padfield, T. and Landi, S., (1966). 'The light-fastness of the natural dyes', *Studies in Conservation,* IIC, 11, No. 4, 181-196; (1966). Giles, C. H., (1965). The fading of colouring matters, *IIC 1964 Delft Conference on the Conservation of Textiles Collected Preprints,* 2nd Edn., pp. 8-26; Privalov, V. F., Bobkova, V. N. and Kuroedova, L. V., (1974) 'Principales lois de décoloration des textes de documents d'archives dans l'obscurité', *Études concernant la restauration d'archives de livres et de manuscrits,* Archives et Bibliotheques de Belgique, Numero Special, Brussels , pp. 243-253.

7. Manufactured by Barcham Green & Co. Ltd. (see address above).
8. Unsupported Lamatec is produced by Ademco Ltd., Coronation Road, Cressex Estate, High Wycombe HP12 3QU, England (1976).
9. Chapman, K., (1976). *Lamatec Archival Tissue Investigation,* HMSO Technical Services Laboratory Report, No. 7, April.
10. Texicryl 13-002 is available from Picreator Enterprises, 44 Parkview Gardens, London NW4.
11. Available from the above supplier.
12. Das Gupta, R. and Whitefield, B. D., (n.d.). *Document Preservation — Archival Permanence of Texicryl laminates,* HMSO Technical Services Laboratory Report, No. 95.
13. Though based primarily on Sankskrit sources, for pigments and other materials (including a recipe for verdigris on p. 22) used in the execution of manuscripts from the Mughal and other Indian Islamic traditions the following is useful: Agrawal, O. P., 'A study in the techniques and materials of Indian illustrated manuscripts,' *Preprints of The International Council of Museums Committee for Conservation Plenary Session,* Amsterdam, September 1969.
14. Plenderleith, H. J. and Werner, A. E. A., (1971).*The Conservation of Antiquities and Works of Art,* 2nd Edn., London, New York and Toronto. 'The black sulphide may be readily oxidized by hydrogen peroxide to lead sulphate which is white and thus it is possible by simple treatment to remove the staining and restore the brilliancy of the white pigment. In the case of red lead that is superficially blackened, treatment by hydrogen peroxide results in the formation of a thin white veil of lead sulphate covering, but not concealing, the red pigment, and as it is unusual for red lead to be converted more than superficially to sulphide, the hydrogen peroxide treatment is generally all that is required to effect restoration.' . . . 'After hydrogen peroxide treatment there is much less chance of the white lead being blackened in future, because the sulphate is less susceptible to change than the basic carbonate.'
15. For further details of the properties and industrial applications of soluble nylon see, *Calaton CA: A Synthetic Resin Finishing Agent for Textiles,* ICI Auxiliary Products Literature, No. 96, First Edition, June 1960; *'Maranyl': Technical Data,* Moulding Powders Technical Service, ICI Plastics Division, Welwyn Garden City 3.6.1966 ('Maranyl' nylon compound C109/P is available in the United Kingdom from ICI Plastics Division for non-textile applications and ICI Dyestuffs Division for textile applications under the trade mark 'Calaton' CA. It is offered for both textile and non-textile applications overseas by ICI Dyestuffs Division under the trade mark 'Calaton' CA.').

(For further observations on Calaton's properties in conservation use see: De Witte,

E., (1975). 'Soluble nylon as consolidation agent for stone,' *Studies in Conservation,* IIC, **20**, No. 1.)

Acknowledgements

Many thanks are due to Melvyn Jones who produced the line drawings.

2.3
Alkaline Buffering

2.3.1 Aqueous deacidification of paper

Vincent Daniels

Aqueous deacidification is a routine operation in paper conservation. The effects of water on paper fibres is considered and the deacidification of paper by water alone is reviewed. The various conservation treatments currently used are looked at with a chemist's eye and some attempt is made to list the relative advantages of these treatments. However, we must rely on the historical evidence present in surviving old papers since accelerated ageing tests cannot be entirely trusted.

One of the chief landmarks in paper conservation thinking was that acidic impurities in paper were detrimental to its permanence, the relevant facts being known as early as 1891. In addition it was reported[1] that acids in paper could be divided into three groups: (a) the acids that were present when the paper was made, (b) the acids produced during ageing processes and (c) acids absorbed onto the paper from the air, i.e. atmospheric pollutants. This view is still held today.

This hypothesis was very useful in explaining why some papers last longer than others. Although there are often anomalies to the rule about acidity and the permanence of paper, the view is still held that deacidification is a good thing. The subject was first investigated in a quantitive manner by Barrow[2] who introduced the term pH into the conservator's vocabulary. The concept of pH and its relationship with hydrogen ion concentration should be familiar to all paper conservators so this will not be dealt with. Barrow demonstrated that a 'neutral pH' was desirable in paper and as the pH of the paper decreased, the rate of loss of strength increased. Folding endurance was used to indicate the strength of the paper and accelerated ageing tests were used to predict the long term performance of the papers used in his experiments. A series of old papers was examined for strength and pH and it was found that there was the expected correlation.

Figure 2.80 shows some of Barrow's data[3] where he plots the retention in folding endurance strength of artificially aged papers against the pH of a cold water extract (before ageing). For some reason Barrow was forced to draw a straight line through these points neglecting everything about pH 6.0. However, it can be seen that the points fall on a smooth curve which could be plotted so that they do fall on a straight line *(Figure 2.81)*. In fact, a graph of retention against hydrogen ion concentration is almost a straight line. There is a great deal of scatter of the points between pH 4 and 7 which indicates that pH is not the only controlling factor.

Acidity in paper is one of the major factors in the degradation of paper and this has been amply demonstrated. Other degradation mechanisms will probably be discovered in the next few decades, but these may be of lesser importance. Photochemical reactions are of importance in some instances.

Having accepted the fact that excess acidity is harmful to paper, it follows that it is advantageous the neutralise the acids present. A scientist un-

familiar with the terms used in paper conservation would ask how we can talk about the pH of paper, a solid material because pH is only meaningful in aqueous solutions. The answer is that the pH really refers to the hydrogen ion concentration in an aqueous extract of the paper. An example of this type of measurement is given in *Tappi* (T529), a précis of which is that: 1.0 g of paper is macerated in 20 ml of distilled water, a further 50 ml of water is added and after one hour the pH measured with a glass electrode. It is evident from this description that paper could be washed free of water soluble acids and a subsequent pH determination would give the pH of distilled water only, i.e. deacidification will have taken place. In one instance [4], after one hour of washing a paper of pH 3.5, the pH was increased to 5.02. This corresponds to a 97% removal of soluble acids, (assuming they were strong acids). Thus it would seem that water washing was an effective method of deacidification.

There is one type of acidity which cannot be washed out of paper because the acid moiety is attached to the cellulose molecule. Cellulose contains hydroxyl groups (– OH), some of which can be oxidised to form a carboxylic acid group, ($-CO_2^-H^+$). This is a source of hydrogen ions. There is evidence that this type of acidity is detrimental to paper permanence, however it can be neutralised by alkalis. When there is a large amount of this type of oxidation the cellulose is called oxycellulose.

Parks and Herbert [5] have found that various oxycelluloses which have had their protons (H^+) exchanged for metal ions have distinctive cold water extract pH's. An aluminium pulp gives pH 5.3 and a calcium pulp gives pH 6.3 despite thorough washing.

Most conservators are not content to rely on water alone for deacidification, but prefer to use an alkaline solution which will convert the acids to soluble or insoluble salts. Many treatments are water based, but others are non-aqueous. As water is a common factor in all aqueous deacidification treatments its effects on paper fibres will be considered in more detail.

Good quality paper is traditionally made of processed vegetable fibres which contain a large proportion of cellulose. Other constituents include fillers, size, colouring and other impurities accidentally or intentionally added. When the relative humidity increases, the cellulose fibres absorb water and they swell. This type of behaviour is illustrated in *Figure 2.81* for cotton fibres[6]. Although any dimension of the paper does not change by more than 2%, individual fibres can increase their diameter by 20% and their length by

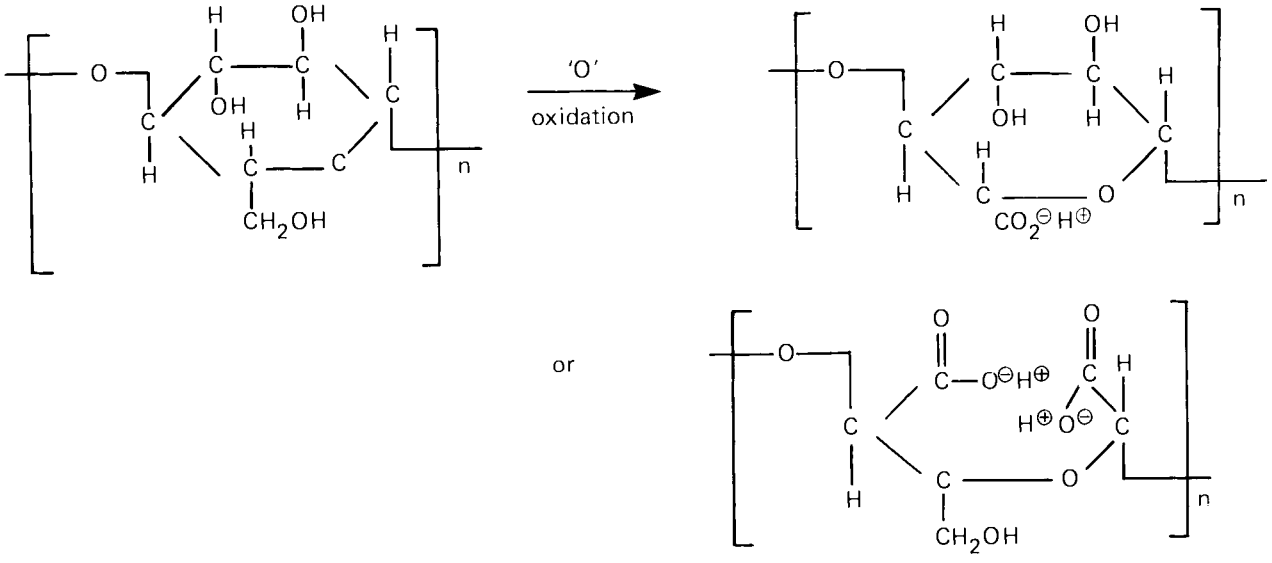

Figure 2.80. Some oxidation products of cellulose.

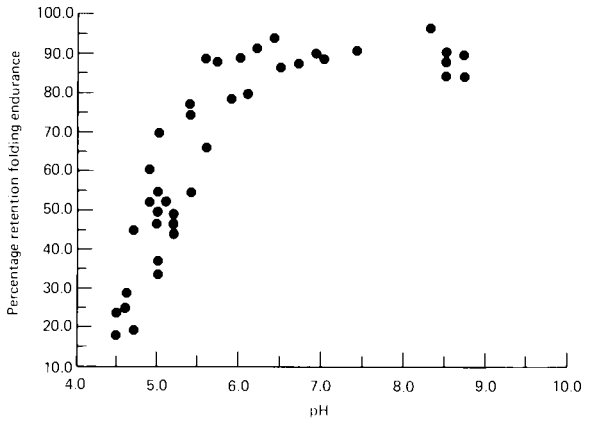

Figure 2.81(a). Barrow's plot.

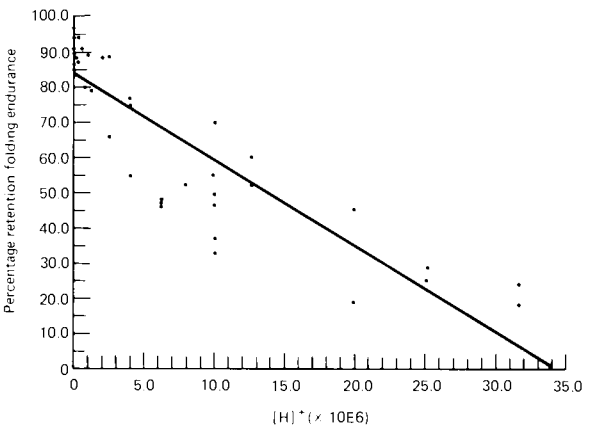

Figure 2.81(b). Daniel's plot.

1%. This corresponds to a 40% increase in volume. Thus when a piece of paper is immersed in water the fibres swell and water enters between the fibres to loosen the bonds between them and provide a method of transport for soluble substances away from the fibres. This degree of swelling is not found for any other common solvent and it decreases on progressing through the series of primary alcohols, methanol, ethanol, etc. Swelling is thought to facilitate the passage of water soluble molecules in and out of the fibres. It has been estimated[7] that fibres dried from water have an internal surface area of about 1 m^2g^{-1} while water-swollen fibres have an area of up to 200 m^2g^{-1}. This increase in available surface area should lead to better washing when using aqueous treatments.

Acidic impurities in paper are thought to be harmful because the acid catalyses hyrdolysis of the cellulose molecules causing a decrease in length with a corresponding loss of mechanical strength. Cellulose is a polymer with a degree of polymerisation (DP) of 5000-10000 in natural unprocessed fibre and 500-1500 when converted into paper. If

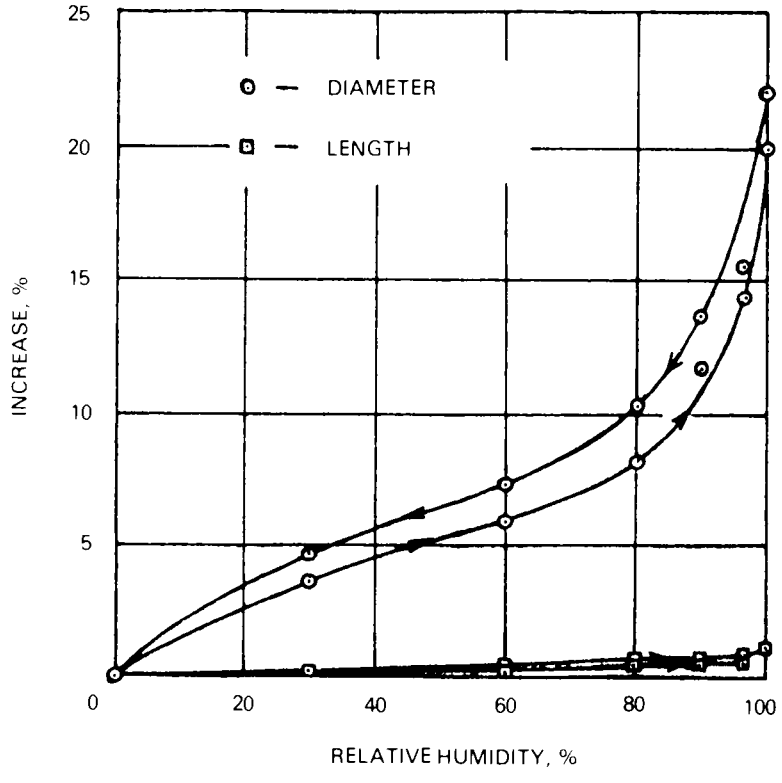

Figure 2.82. Dimensional changes of cotton during sorption of water (5).

the DP is decreased to below 200-250 the fibres disintegrate on handling. Alpha-cellulose corresponds roughly to cellulose with a DP of greater than 200-250[6]. It is often found that the alpha-cellulose content of naturally aged, weak papers is as high as that of modern papers[8]. Brittle palm, leaves and papyrus yield a high-alpha cellulose content too. These results have led some workers to suppose that there are other mechanisms whereby acids reduce the strength of paper. The mechanical properties of paper depend not only on the strength of the individual fibres but to a large extent on the fibre linkages[9]. These bonds form during the drying stage when the paper is made. The fibres overlap in many places, as the SEM picture in *Figure 2.83* shows. This picture is of a piece of filter paper and it can be seen that the main fibre plays a small part in holding the sheet together and that there is much overlap between the beaten out parts of the fibre. When an old piece of paper is wetted there is a chance that on redrying the inter-fibre bonds can be partially remade. Little systematic work has been done on this aspect of aqueous treatments, but Barrow has reported that he was surprised to find that the folding endurance strength of several papers increased when spray wetted and subsequently dried. Textile conservators have expressed the view that cotton and linen objects are stronger after being washed in water. It should be remembered at this stage that water can wash away soluble products of ageing reactions from paper. If these are brittle substances they can decrease the folding endurance strength of the paper and these can be coloured compounds which can cause a displeasing aesthetic effect. Thus washing can cause pleasing mechanical and visual effects.

Wilson[10] has shown that some types of metal ions in combination with oxycellulose are more stable than others. Work with differential thermal analysis has shown that at around 110°C and at 300-400°C the aluminium form decomposes at a lower temperature than the free oxycellulose and the calcium form decomposes at the highest temperature. These results reflect the way we think about metal ions in paper, i.e. that aluminum ions destabilize paper while calcium ions stabilize it.

Arney *et al*[11] have shown that both hydrolysis of cellulose and oxidation of cellulose are slowed down by deacidification with calcium carbonate.

Now that some of the relevant facts about deacidification of paper are known, it might be possible to choose between the various processes available. An ideal treatment would:

(1) Remove all soluble acids or convert any acid to a harmless product.
(2) Leave a harmless residue of neutralizing agent which will maintain a pH of about 7.0 to 8.5.
(3) Be harmless to conservators and future users of the paper.
(4) Be inexpensive and easily applied.
(5) Have been present in paper for thousands of years so that there is no need to perform accelerated ageing tests to predict its performance.
(6) The treatment should not harm the object in any way or detract from its value as documentary or technological evidence.

There are no treatments which meet all of these requirements, but some meet most of them. Condition (6) is broken by almost all active conservation treatments as some of the object is changed to make it cleaner or more stable.

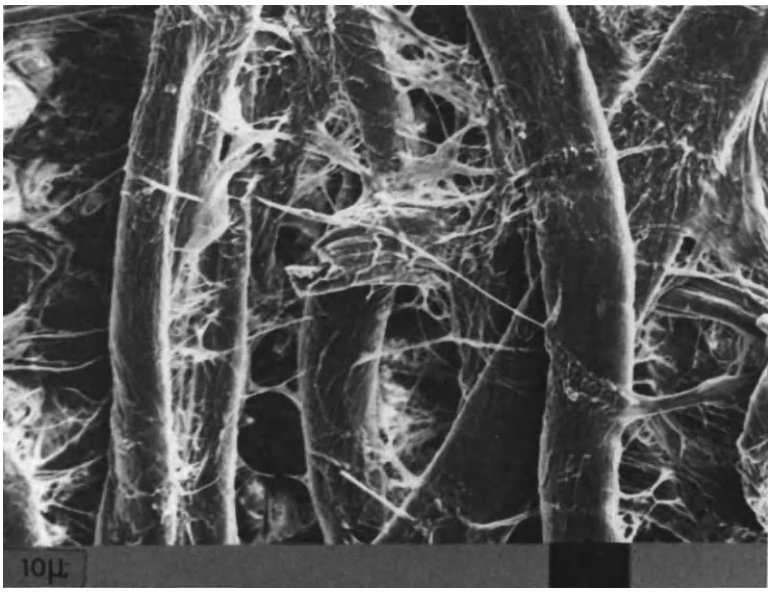

Figure 2.83. A scanning electron micrograph of a piece of filter paper. (X1000).

Treatments in use will now be examined from a chemist's viewpoint. Practical methods are well known and are described elsewhere. It should be noted that as far as health and safety is concerned water is very safe material. No special skills or apparatus are required to handle it and it is not flammable or toxic. This contrasts with some non-aqueous systems. The methods of deacidification are meant for single paper sheets and care must be taken when real documents are used as the writing and drawings on the surface are very important. Whole books are still more awkward to treat as there are cockling, penetration and drying problems.

Calcium hydroxide

A saturated solution contains 1.85 g/l in cold water and has a pH of 12.4. Sulphuric acid, which is supposed to be the main source of acidity in paper stored in an industrial environment, is converted by deacidification using calcium hydroxide into *nearly insoluble* calcium sulphate. Paper is immersed in the liquid and when it is removed, the calcium hydroxide reacts with carbon dioxide in the air to form calcium carbonate, a substance which is often present in well preserved old paper.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Accelerated ageing tests also show that this is a good deacidifying treatment. However, Barrow showed that in some cases the folding endurance can be decreased after this method of conservation. One possible disadvantage to this treatment is the high initial alkalinity of the solution. In some cases organic dyes can change colour. Under this heading we can include iron-gall ink, which can become paler, and certain red inks can become soluble. The high alkalinity is temporary and the pH of the paper drops to about 8 when the calcium carbonate is formed.

A modified version of this treatment is to immerse the paper in two solutions, one of calcium hydroxide followed immediately by one of calcium bicarbonate. This process precipitates a larger amount of calcium carbonate in the fibres.

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + 2H_2O$$

This is known as the Barrow two-stage process. Both of these deacidification processes are as harmless to operators as a process can be.

Figure 2.84[4] shows a piece of filter paper which has been treated with calcium hydroxide solution. It can be seen that there are crystals of calcium carbonate present and doubts have been voiced that this localized deacidifying agent may not be effective. Energy-dispersive X-ray fluorescence shows that even in places where there are no calcium carbonate crystals there is at least 5% of calcium present on the surface of the fibre.

Other hydroxides

Alkaline hydroxides which have been proposed as deacidifying agents are potassium, sodium and barium hydroxides. In theory all the hydroxides of the Group I and II elements in the periodic table could be considered, but undesirable properties such as high radioactivity, insolubility, toxicity or cost prevent this. Barium hydroxide, widely used in methanol solution [12], could be used in water and has a higher solubility than calcium hydroxide.

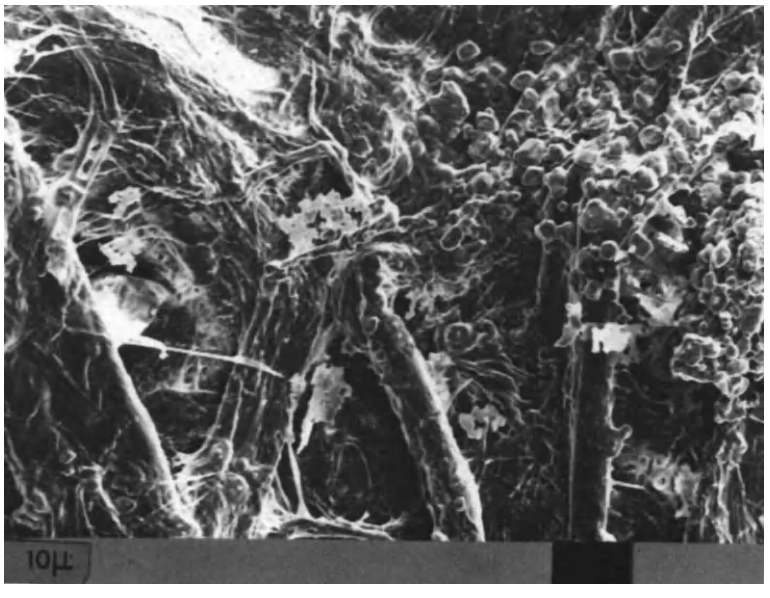

Figure 2.84. A scanning electron micrograph of a piece of filter paper deacidified with calcium hydroxide solution and allowed to dry (×1000).

However, its toxicity is a problem and it is difficult to see any advantage over using calcium hydroxide. Barium hydroxide would ultimately react with carbon dioxide in the air to form barium carbonate. Sodium hydroxide is a strong alkali but there seems little advantage using it when the bicarbonate is soluble in water and readily available. (0.01M sodium hydroxide has a pH of 12.0, 0.01M sodium carbonate has a pH of 7.3). The author knows of no experiences concerning the use of potassium hydroxide or its bicarbonate, but the bicarbonate is hygroscopic, i.e. it absorbs water from the air so its use would produce problems.

Bicarbonates

Some bicarbonates are sufficiently soluble in water for them to be used as deacidifying agents. The pH values of their solutions are not as high as the corresponding hydroxides. When large amounts of carbon dioxide are present in the solution the pH can be on the acid side because there is a mixture of the bicarbonate and carbonic acid. Thus it is possible to deacidify using acid solutions. When calcium and magnesium bicarbonate solutions are prepared for deacidification purposes they are made by bubbling carbon dioxide through a suspension of the relevant carbonate, e.g.

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$

This emphasizes the acidity of the deacidifying treatment.

The magnesium bicarbonate method has been proposed by Barrow as a spray deacidification process. His accelerated ageing tests have shown this to be as good a treatment as using calcium hydroxide. Magnesium bicarbonate is about ten times as soluble as calcium bicarbonate so more can be put into the paper. Magnesium bicarbonate converts to magnesium carbonate when it is dried onto the paper. Magnesium carbonate coexists with calcium carbonate on many old good-quality papers, which is a strong point in its favour.

Sodium salts can be put into paper as alkaline buffers, and there is some controversy as to whether sodium ions can be harmful to cellulose. The author's own opinion is that any excess alkalinity is harmful to paper but the point where this happens probably varies with the metal ion present. With calcium and magnesium this does not happen until about pH 10.5, while with sodium it may happen at pH 9.5.

Some of the arguments are as follows: Sodium bicarbonate or sodium sequicarbonate in the form of Natron has been shown to have preserved ancient Egyptian linen bandages in a remarkably fresh state[13]. Accelerated ageing tests will not work on this bicarbonate, as it decomposes to the more alkaline carbonate (a 0.01M solution has a pH of 10.5). The author has been informed that sodium borate gives good results as a deacidifying agent, in dry and humid accelerated ageing tests on paper[14]. As a textile treatment borax has not so far been shown to cause ang degradation. On the other hand, Hey[15] predicts that sodium ions are harmful and Koura and Krause[16] show that paper with sodium ions at pH 10 is less stable than paper at pH 4 with no metal ions.

Alkaline salts and buffers

Salts of a weak base and strong acid are acidic in aqueous solution; an example of this is alum (aluminium sulphate), thus alum impregnated paper is considered to be acidic in ambient conditions. On the other hand, a salt of a strong base and a weak acid is alkaline in an aqueous solution. Examples are sodium acetate and sodium borate (borax). Borax has a pH of 9.2 in a 0.01M solution. A solution of borax or borax plus the free acid (boric acid) can be termed a buffer solution since its pH does not change very much when diluted or when small amounts of acids or alkalis are added. Borax has been used as a deacidifying agent in paper. The list of alkaline buffers which have been suggested for use in paper has been extended by Russian workers[4] who have produced evidence that alkaline salt buffering is a suitable treatment for paper. Buffers suggested include:

0.05M $Na_2B_4O_7\ 10H_2O$ + 0.2M H_3BO_3

0.067M KH_2PO_4 + 0.067M $Na_2HPO_4 2H_2O$

These are all crystalline, colourless substances that impregnate the paper fibres. Thus small amounts of acidic impurities are dealt with by a buffering action as are subsequently absorbed acidic gases like sulphur dioxide. It should be remembered that the above chemicals are water soluble and remain so. In regions of high humidity the salts could migrate to the surface of a leaf and precipitate on the surface in the same way as salts migrate to the surface of a stone sculpture or pot.

Summary

There are many things we do not know about the deterioration of paper, and the effects conservation treatments have on paper. However, we cannot stop doing conservation treatments because of this, as Cardinal Newman said, 'A man would do nothing

if he waited until he could do it so well that no one could find fault with what he has done.' If pH was the only variable in changing the rate of deterioration our task would be easy and all aqueous deacidifying processes would more or less equally effective. Complications arise from other causes, e.g. the fact that metal ions such as calcium and aluminium can enter into the reaction scheme and change the stability of the paper to oxidation by acid hydrolysis and perhaps by other means. While much useful evidence can be obtained from performing accelerated ageing tests on paper deacidified in various ways, these tests are unreliable and can lead us to false conclusions. Thus we must rely heavily on the analysis of good-quality old papers to guide us in the right direction. Calcium and magnesium carbonates have been incorporated in paper for many hundreds of years and confer stability on these papers. It is this historical evidence that gives weight to the opinion that while other deacidifying treatments may seem to be as effective, the incorporation of calcium and magnesium carbonate should be used in preference to other chemicals. Of course, in many cases it is expedient to use one of the newer methods and these, so far, have produced acceptable results. It is to be hoped that in the next few decades we will have sufficient information about paper degradation to make a better judgement. As Julius Caesar said, 'Good reasons must, of force, give place to better'.

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2.3.2 Non-aqueous deacidification of books and paper

George B. Kelly, Jr.

The problem of mass deacidification of books and papers is examined and the requirements for an ideal process are quoted. The mass deacidification processes currently available are reviewed. A liquid process based on magnesium methoxide and two gaseous processes based on morpholine or diethyl zinc appear closest to commercial status at this time and are described in some detail with their advantages and disadvantages. Overall, the diethyl zinc process, as developed at the Library of Congress, while it does require extraordinary safety precautions in the processing, appears to be the most promising in terms of permanence of the treatment and minimal side effects. Non-aqueous deacidification processes available to the individual conservator are also briefly discussed.

Mass deacidification

The problem of acid deterioration of books and papers has been recognized for many years. As the libraries began to accumulate more and more books that were so degraded they could no longer circulate, the problem attracted increasing attention and various remedies and treatments have been proposed. As early as 1936, Schierholz was granted a patent for the use of alkaline earth bicarbonates for the stabilization of paper. Many of the treatments that have been proposed are excellent, but most were developed with the idea of use by an individual conservator treating relatively small amounts of paper or single books.

In recent years, it has been recognized that the problem is beyond the scope of the individual conservator. The Library of Congress has an estimated six or seven million books which are so deteriorated that they should not circulate, and with some exceptions, the whole collection should be neutralized and buffered, or in popular terminology, deacidified. At a pound a book, there are at least 3000 tons of books to be treated. While we have no figures for the United States total, there must be at least 100 times as many, or 300,000 tons to be treated, and this is just the start. There is a pressing need for a mass treatment process as simple as ethylene oxide fumigation to arrest the degradation.

For an ideal process there are some stringent requirements that should be met. These are:

(1) The book must be penetrated completely in a reasonable period of time.
(2) The paper must be uniformly neutralized.
(3) The paper must be buffered at a pH of 7 to 8 for minimal effect on inks and colours.
(4) The paper should be given an alkaline reserve equivalent to 3% calcium carbonate for maximum permanence.
(5) If the treatment is introduced as a gas, it must not come back out of the book or paper. This implies some sort of reaction to change the nature of the gas used — possibly a reaction with cellulose or a polymerization to a non-volatile product.
(6) The treatment should not leave an odour in the book.

(7) The treated paper should be non-toxic to humans.
(8) No new problems should be introduced such as darkening of the paper or attack on leather.
(9) The treatment should be economically feasible.
(10) The expected life of the paper should be significantly improved.

In response to the evident need, several processes for mass deacidification have been proposed. These are exclusively non-aqueous processes, as attempts to treat books with water-based processes led to severe damage to the bindings due to the swelling of the paper. Some water may be tolerated depending upon the process, but the quantity must be severely limited.

Mass treatment processes are of two types — liquid based (discussed in section 2.3.3 by Richard Smith, Mass reacidification at the Public Archives of Canada) and gaseous or vapour based.

Gaseous or vapour deacidification

There are a great many volatile organic compounds which appear to be alkaline enough for a vapour-phase mass deacidification process, but only a very few appear to be practical. Some are far too toxic, some have too little volatility, some cause undesirable side effects such as discolouration and some are ineffective. Those that have been proposed and investigated fall generally into two groups; ammonia and its derivatives the amines and the organo-metallic compounds.

Ammonia itself was investigated by Kathpalia.[1] Langwell investigated cyclohexylamine carbonate and proposed a very simple scheme in which papers impregnated with this compound would be interleaved at intervals in a book so that the vapours could permeate through the pages and deacidify it. This method was discussed extensively in *Restaurator*.[2] The Barrow Laboratory investigated the use of several amines and finally settled on morpholine as the vapour phase-treating agent.[3]

In general all of the amines and ammonia function similarly so we will discuss only one — the Barrow morpholine process — as an example of all. This method has been extensively tested by work at the Virginia State Library by Barrow personnel.

In the morpholine process the books are evacuated in a vacuum chamber and a mixture of morpholine and water is vaporized into the chamber which is kept warm to prevent condensation. The chemical vapour is forced into the books by cycling the pressure over a range of 30-40 mm Hg for a relatively short time, 10 min or less. The concentration of the morpholine and the exposure time must be closely controlled to avoid excessive absorption by the covers which results in plasticizing the pyroxylin or plastic coatings and making them sticky. The books are removed and aerated to remove excess morpholine, which has an unpleasant odour and causes definite discomfort if one is exposed to the vapour for any significant length of time.

The amine penetrates the books well and deacidifies them but the treatment is not permanent.[4]

Because of the reversion to an acid status with time, the treatment would have to be repeated every few years to maintain protection. The amines also may cause significant discoloration of papers, the amount depending upon the particular amine and the type of paper.

The tendency for amines to leave the paper after treatment led the Library of Congress and the Dow Chemical Company to investigate ethylene imine as a gaseous treating material as it could be introduced as a gas and then easily polymerized to a non-volatile polymer or reacted with the cellulose to form an aminoethylated cellulose. Despite the fact that the paper could be deacidified and buffered at a pH of 8.7 with additions of as much as 4.5% nitrogen based on the weight of cellulose, no significant improvement in ageing characteristics was achieved with ethylene imine, and the paper was seriously discoloured.

At this point, it was apparent that the amines offered little hope of permanent deacidification, so the attention of the laboratory at the Library of Congress was turned to the organo-metallic compounds. Of these, diethyl zinc offered a unique combination of good volatility, suitable chemical properties, commercial availability and reasonable cost which made it the logical choice for development of a mass deacidification treatment. After five years of development, we now believe the diethyl zinc process is ready for commercial use. Large scale trials of this process have been described in a paper presented at the 6th AIC Annual Meeting in Fort Worth, Texas, in June 1978. At that time, some problems remained, but they have now been resolved.

Briefly, the process consists of drying the books in a vacuum chamber for a period of three days during which time the pressure is reduced to 35μ absolute and the temperature is raised to 45°C to remove all water to avoid the violent reaction of diethyl zinc with water. After isolating the chamber, diethyl zinc is added in an amount equal to 3% of the weight of the books. The pressure rises to about 35mm Hg from the vapour pressure of the diethyl

zinc. After three days exposure to the vapour, the books are completely penetrated, neutralized and buffered. Any excess diethyl zinc is destroyed by the addition of alcohol. When tests show that all diethyl zinc is gone, water is added (about 3% of the weight of the books) and the chamber is raised to nearly atmospheric pressure with carbon dioxide. The moist carbon dioxide is circulated in the chamber with a fan for 24 hours. This insures that the alkaline reserve is in the form of zinc carbonate rather than zinc oxide. (Zinc carbonate does not photosensitize the paper as does zinc oxide.) After evacuation of the chamber to remove the carbon dioxide and the ethane which is a by-product of the treatment, the chamber is refilled with air and the books removed. The complete cycle takes about eight days including loading and unloading.

The chamber used for the large scale tests is shown in *(Figure 2.85)*. It has a capacity of about 5000 books and is located at the General Electric Space Center in Valley Forge, Pennsylvania. There are a number of similar chambers scattered across the U.S.A. These were used in the space programme and now should be available for book treatments as the reduced emphasis on the space programme has left most of them idle.

The preferred chamber packing is with the books in the spine-down position, as this appears to be the most efficient for drying and penetration. It is important that the books be packed somewhat loosely, and that separators such as screen wire (½ in. mesh) be placed between the books to avoid the formation of deposits on the covers *(Figure 2.86)*.

The treatment achieves a pH of 7.8 and an alkaline reserve of about 2% zinc carbonate in the books, which makes it one of the mildest available. The mildly alkaline pH makes the process particularly attractive for treating maps where a low alkalinity is desirable for minimal effect on the colours. More than 100 maps covering a wide selection of colours, ages and types of material and backings have been treated in stacks of 20 to 30 maps with each stack enclosed in a map folder, with no evidence of damage or colour change in any map. The bindings and covers of books also have shown no evidence of damage in tests including leather, vellum, plastic, cloth, pyroxylin and board covers, some of which were highly decorated.

In testing the performance of the treated papers with accelerated ageing tests, some anomaly was noted in papers containing large amounts of groundwood. These performed very poorly in dry ageing tests at 100°C but did well in humid ageing tests at 90°C and 50% RH. All other papers did well in both dry and humid ageing tests. Since it would be rare for books to be stored in an atmosphere as dry as that in the dry ageing tests (2%RH), the performance at room temperature should parallel the results in the humid ageing tests. In general, the treated books and papers show an estimated life of about four to five times that of untreated copies.

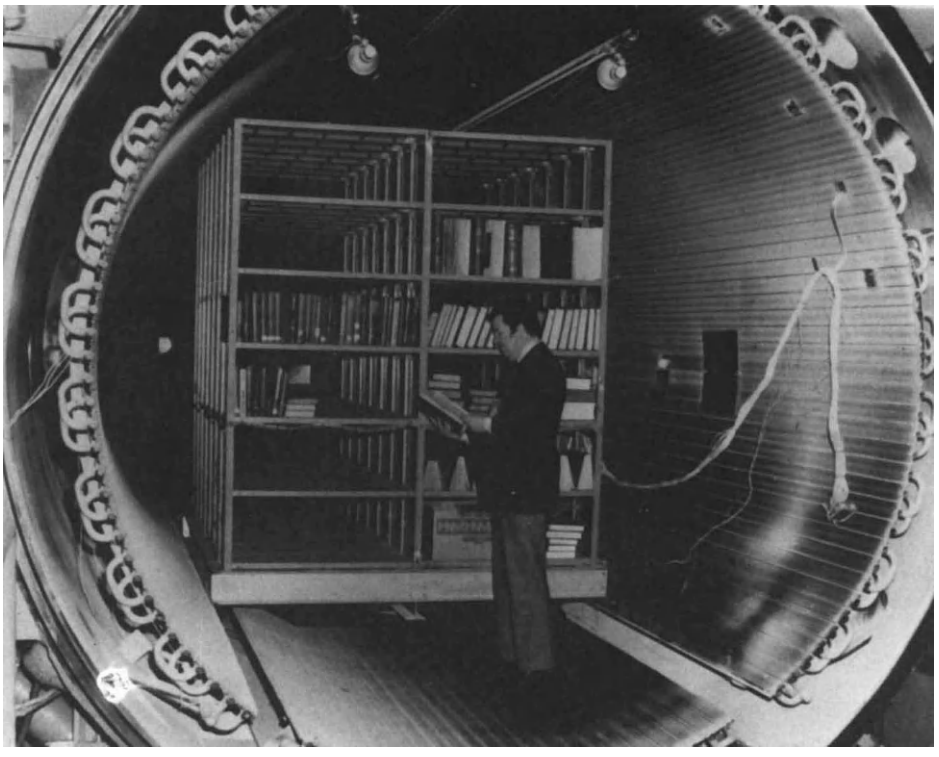


Figure 2.85. Chamber at GE Space Center.

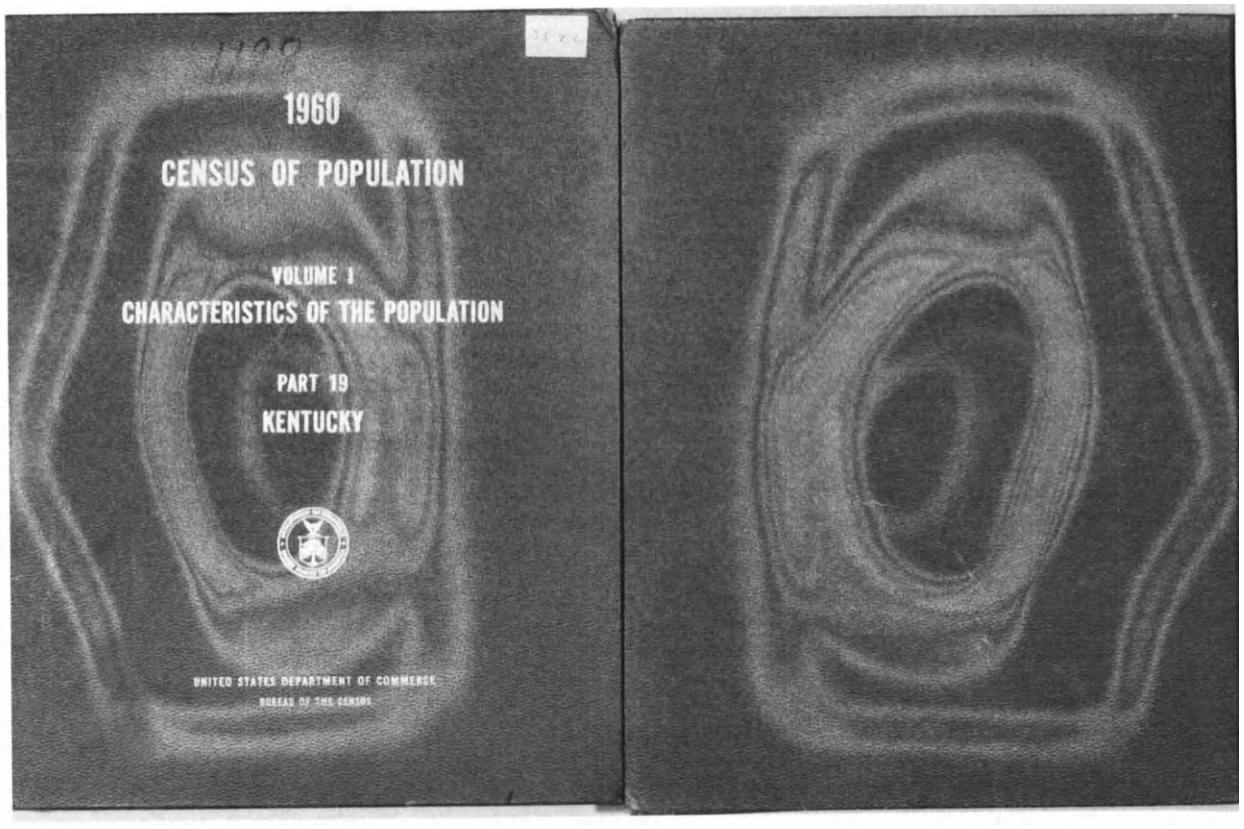


Figure 2.86. Bookcovers from DEZ treatment without spacers.

At this point the process was considered ready for commercial use and a full-scale, 5000-book run was scheduled to demonstrate the feasibility before starting to treat the collections. The cost was estimated at $6.00 per book in the full-scale operation (all costs given in this paper are as of 1980). However, just as preparations were being made for the run, the manufacturer of the diethyl zinc, Texas Alkyls, Inc., stated that they now considered diethyl zinc too dangerous to ship in undiluted form or in any solution concentrations above 15%. This was due to the fact that if the container were exposed to a fire, there was no way to vent it fast enough to avoid an explosion with a high concentration of diethyl zinc present because the decomposition temperature of diethyl zinc was only 150°C.

Although a 400-book run had been made with dilute diethyl zinc, operation with a 5000-book load would be impractical both from a safety standpoint and from the necessity of disposing of such large volumes of diluent after the treatment. Because at a 400-book treatment level, the process would be completely uneconomical, it appeared that no further progress could be made.

However, all may not be lost, as the manufacturer of the diethyl zinc has come up with a stabilized mixture that is safe to ship. We feel that the prospects for success are bright, and if the tests with the new mixture go well we can carry out our 5000-book demonstration run early next year, and, depending upon our budget, possibly begin treatment of the collections in 1982[5].

In view of the intense interest in and serious research that has gone into the subject of mass deacidification in recent years it appears unlikely that any radical new developments will appear in the foreseeable future. All that remains is to take up the problem of finding sufficient funds to accomplish the task of deacidification. The alternative is to continue to watch our library volumes crumble into dust.

Now the diethyl zinc process may be fine for large institutions or a co-operative venture, but what of the individual conservator with neither the capital nor the technical training to employ such a potentially hazardous process? It has been seen that the cheap and simple mass processes based on amines or ammonia are, at best, temporary treatments, and the liquid mass method is still not commercial, so the individual conservator must continue to use the traditional one-at-a-time treatments.

The aqueous treatments based on the Barrow process are very effective, but tend to be somewhat slow due to the care required in handling the sheets that have been weakened by being wet with water

and the time required to dry the sheets. Nevertheless, these processes are generally used for most deacidifications by individual conservators and also for much of the paper and manuscript deacidification at the Library of Congress because of their safety and reliability. However, in recent years the Library has been turning increasingly to the use of non-aqueous systems in deacidification. These have long been used in the treatment of delicate papers because the sheets are not weakened as they are when wet with water. Furthermore, the papers usually do not wrinkle on drying when using the non-aqueous systems.

One feature that has not been appreciated previously is the rapidity with which the non-aqueous systems penetrate the paper and the extreme rapidity with which the sheets can be dried. This increases the rate at which the sheets can be processed and in many instances the saving in time more than outweighs the increased cost of the non-aqueous system, which in our case runs about $5.00 per gallon. We have made extensive use of these at the Library of Congress — most recently in the treatment of a large collection of county atlases which is still in progress. No problems have been encountered in the county atlas treatment with any of the inks or colours, but difficulty with ink solubility and colour changes are always possible, so careful testing is necessary before each use.

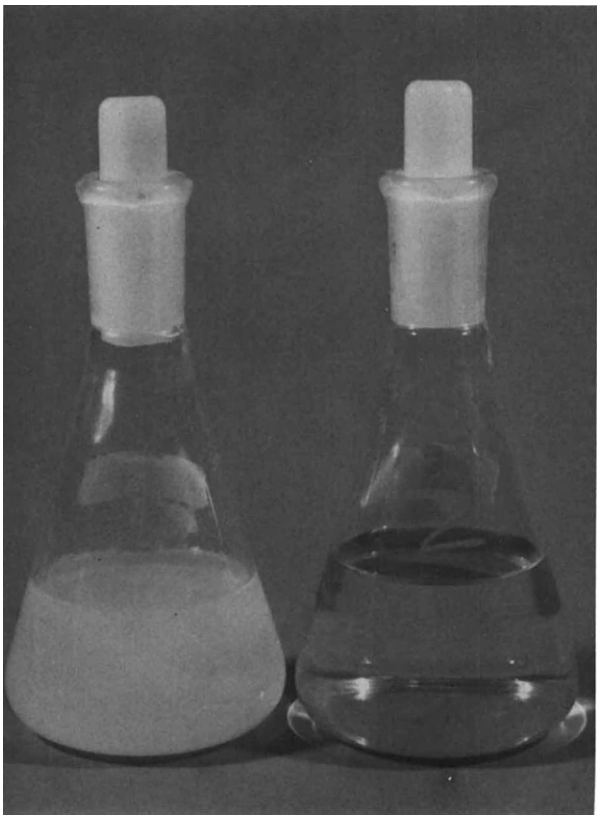


Figure 2.87

The most convenient non-aqueous deacidifying solutions that have been found are based on magnesium. Magnesium methoxide is purchased as an 8% solution in methanol and this is diluted to about a 0.7% solution with trichlorotrifluroethane, which is available under several names such as Freon TF. This mixture has the property of not only giving a very quick-drying solution, but the fluorocarbon solvent has a very low solubility for inks, reducing the tendency for the methanol to cause the inks to run. Occasionally problems are encountered with inks or colours with these solutions, but not very often.

Now magnesium methoxide is a very effective neutralizer, but it is very sensitive to water, so on damp days or with somewhat damp paper, the solution tends to precipitate prematurely and leave surface deposits on the treated paper — a rather annoying occurrence. It has been found that saturating the solution with carbon dioxide converts it into methyl magnesium carbonate, and this is much less sensitive to water, although it is just as effective in deacidification. A comparison of the two solutions is shown in *Figure 2.87*. The solution of magnesium methoxide in methanol was completely precipitated by the addition of 0.5 ml of water, whereas the equivalent solution of methyl magnesium carbonate absorbed 5 ml of water without precipitation, and was still suitable for use.

Either solution is equally effective as a deacidifier and both produce adequate alkaline reserves in the paper as shown in *Table 2.20*. Both leave magnesium carbonate as the alkaline reserve. The only advantage of the methyl magnesium carbonate is that it is easier to use when humidity is a problem. Application equipment is slower to clog, and there is less tendency toward surface deposits, and usually a significantly better shelf life. However, even the methyl magnesium carbonate can be precipitated if it absorbs enough water, so it must be handled with reasonable care and kept well stoppered. Containers is use should be kept covered as much as possible — particularly in the draught of a hood where the rapid evaporation of the Freon chills the solution to the point where it begins to condense water out of the air and it soon precipitates.

These solutions are toxic due to the methanol content, and thus should be used in a hood for safety. The solvents also tend to dry out the skin, so rubber gloves are advisable, and eye protection as well, as the solution can be very irritating to the eyes.

The preparation of the methyl magnesium carbonate is simple. The solution of magnesium methoxide of the required strength is simply subjected to

a slow stream of carbon dioxide for 1.5 hours. Using a ¼ in tube in a 5 gallon carboy, the carbon dioxide bubbles should be coming about as fast as one can conveniently count. Heavier flows only waste carbon dioxide without any concurrent benefits. A precipitate may be noticed forming in about 20 min but it will redissolve on continued carbonation, and when the solution is again clear it is ready for use.

The magnesium methoxide solution as purchased may be somewhat yellow, or become so on storage. This may be due to iron from the can used by the supplier. It is recommended that only containers with an epoxy liner be accepted. These have been used over a period of 6 to 8 months with no iron pick-up, whereas the usual tinned iron cans pick up significant iron within a few weeks after the seal is broken. It is also found that a yellow colour sometimes develops that is not due to iron, and this is no problem as it disappears when the solution dries. So any yellow solution has to be tested for iron. Take 1 or 2 ml, make acid with dilute hydrochloric acid and add a drop or two of 4% solution of potassium ferrocyanide; a blue colour shows the presence of iron, and indicates that the solution should not be used in restoration work. One way to prevent iron pick-up is to transfer the magnesium methoxide solution to glass or plastic containers as soon as it is received, but be sure to make the transfer on a day with low humidity and seal the containers well.

Unfortunately, there is nothing radically new in the deacidification processes for individual conservators. However, it is hoped that the development of mass-deacidification processes will take care of the great bulk of material needing deacidification and leave the conservators to handle the particularly valuable items or those needing special attention. In this way the general collections may be saved and the valuable items can receive the special attention they deserve.

Table 2.20 Non-aqueous deacidifiers properties of treated papers.

Paper Number	Treatment	pH	Alkaline Reserve $MgCO_3$ (%)	MIT Fold ½ kg MD	MIT Fold ½ kg CD	Thickness (mm)	Brightness (%)	Fold retention After ageing[a] (%) MD	Fold retention After ageing[a] (%) CD
1	None, control	6.5	None	558	470	0.097	74.5	16	23
	Mg methoxide	9.1	3.67	532	549	0.122	74.6	46	64
	Mg methyl carbonate	8.9	3.17	483	691	0.098	74.0	56	52
2	None, control	6.1	None	565	316	0.086	75.4	15	22
	Mg methoxide	10.2	3.42	670	449	0.107	75.4	46	38
	Mg methyl carbonate	9.8	3.47	575	448	0.091	73.0	50	40
	Solvent only	6.5	None	593	226	0.092	76.6	23	31
3	None, control	5.3	None	5499[b]	—	0.188	78.0	1[b]	—
	Mg methoxide	10.3	4.62	5501[b]	—	0.200	80.9	54[b]	—
	Mg methyl carbonate	10.3	5.12	5237[b]	—	0.194	78.0	48[b]	—

[a] 36 days at 100°C

[b] Handmade sheet, randon fibre orientation

Notes and References

1. Kathpalia, Y. P., (1962). 'Deterioration and conservation of paper, Part IV, Neutralization', *Indian Pulp and Paper*, XVII, No. 4, October, 226-32.
2. Dupuis, R. N., Kusterer, J. E., and Spraul R. C., (1970). 'Evaluation of Langwell's vapour phase deacidification process', *Restaurator*, 149-164.
3. Walker, B. F., (1977) 'Morpholine deacidification of whole books', *Preservation of Paper and Textiles of Historic and Artistic Value,* Williams, J. C. (Ed.), American Chemical Society, 72-98.
4. Furthermore, morpholine is extremely easy to nitrosate, and nitrosomorpholine is a very powerful carcinogen. Considering the vigorous US Governmental efforts to get nitrates out of cured meats, such as ham or bacon, due to the possible formation of nitrosamines in the body, the writer doubts that the Environmental Protection Agency would permit the use of morpholine in library books. It is so easy to nitrosate that nitrogen oxides in the atmosphere of cities would be expected to form significant amounts of the nitrosamine in the books.
5. With regard to the reference to the 5000-book test, it has indeed been carried out successfully. The final tests were performed at the Goddard Space Center near Washington DC by Northrop Services, Inc., a civilian contractor of NASA for whom the writer acts as a consultant. Extensive instrumentation of the NASA Space Chamber used in the test enabled the recording of complete data on the details and progress of the treatment. The books were thoroughly tested by the Library of Congress for complete effectiveness of the treatment, and those responsible were highly pleased with the results.

   With extensive data on the tests, Northrop was able to design a facility to treat 500,000 books per year. The Library is now seeking an appropriation from Congress to build this facility, with good prospets for approval. The facility is presently projected to be in operation by the Autumn of 1984, if the approval is forthcoming. The location would be at Fort Detrick near Frederick, Maryland, because it is relatively isolated, and well equipped to handle chemicals, yet it is readily accessible to the Library.

2.3.3 Mass deacidification at the Public Archives of Canada

Richard D. Smith

This chapter is based on a non-technical coloured slide presentation of the Wei T'o® Non-aqueous Book Deacidification System[1] pilot plant which is located in the Public Archives of Canada in Ottawa. The chapter summarizes that presentation using black-and-white illustrations selected from the same slides. A few of the improvements that have been made since 1980 are noted in the text and a status report updating it is given at the end.

The concepts underlying the Wei T'o® system[1] were developed at the Graduate Library School, University of Chicago between 1964 and 1970. During this period, the author invented and tested mass techniques to deacidify paper and books and for strengthening deteriorated paper in book, as well as other beneficial treatments as components of an all-round preservation process. Sources for information on this work and more recent research are listed in the 'Sources of Further Information' at the end of this article.

In June 1974, Jan Pidek, Chief, Records Conservation, Public Archives of Canada, requested Wei T'o® Associates to submit a plan for a pilot plant test of the deacidification portion of this process. Records Conservation provides preservation services to the Public Archives and the National Library of Canada. The proposal was made and accepted and subsequent support by the Public Archives has made it possible to build this system, the only mass-deacidification system presently in operation in the world.

Work commenced in late 1974 to design, construct, install, test and evaluate the Wei T'o® deacidification process against the criteria set up by the Public Archives and the National Library. Their goals were a deacidification process which would

(1) Be safe and appropriate for operation inside an archives/library building;
(2) Provide affordable and effective deacidification treatment;
(3) Not affect the physical appearance of treated items; and
(4) Establish physical and chemical conditions that would facilitate subsequent strengthening, stablization or restoration treatments.

The deacidification agent utilized in the process is a magnesium alkoxide. It is dissolved in a liquefied gas solvent composed of methanol and dichlorodifluromethane. The advantages of this non-flammable, non-explosive, low-hazard solvent combination are that the combination solvent will clean and rapidly wet closed books, dissolve and transport the deacidification agent, affect relatively few book components detrimentally, can be removed readily from books, can be recovered easily for further use and probably sterilizes the materials as it wets them.

How the process works can be understood by studying the Wei T'o® liquefied-gas deacidification solution itself. Methanol and dichlorodifluoromethane, the organic solvents, are used to dissolve the magnesium alkoxide deacidification agent and carry it into paper. Initially the excess deacidification agent, introduced to protect against future acid attack, forms a mixture of magnesium carbonate and magnesium hydroxide, i.e. dried milk of

magnesia. Subsequently, these two chemicals react further with carbon dioxide and water vapour from air to form basic magnesium carbonate. The magnesium hydroxide is particularly advantageous because it inhibits the trace metals, iron, copper and cobalt, from catalysing oxidative reactions. This inhibition may also keep iron from combining with moulds to produce coloured stains. Magnesium sulphate, i.e. Epsom salts, is the principal chemical deposited when the acids in paper are neutralized. The findings of long-term scientific studies indicate that all of these chemicals and reaction products are beneficial to paper. Moreover, these very same chemicals are introduced into paper by a highly regarded aqueous deacidification process, and they are found in ancient papers that remain in excellent condition today.

In mid-1979, the Wei T'o® non-aqueous book deacidification system was delivered and installed in the Public Archives/National Library building in Ottawa. The fourteen-step cycle originally followed includes three preparatory and eleven treatment steps.

The three preparatory steps are

(1) Screen books for suitability for treatment and load them into wire baskets.
(2) Dry books for 24 hours in a warm air dryer; and
(3) Complete drying in a vacuum dryer overnight.

The eleven treatment steps are

(1) Load two baskets of dried books in the process tank.
(2) Evacuate air from the process tank and books.
(3) Pressurize the process tank and books with recovered solvent vapour.
(4) Fill the process tank with Wei T'o® liquefied gas deacidification solution.
(5) Pressurize the liquid-full process tank to impregnate the deacidification solution throughout the books.
(6) Reduce pressure and drain unused solution from the process tank.
(7) Commence drying by evacuating the process tank to 7 lb/in^2/g and recover and condense the solvent vapours removed.
(8) Complete drying by vacuum, discarding any remaining solvent vapours.
(9) Equalize pressure and purge the process tank with warm air.
(10) Open the process tank, remove deacidified books and seal books inside corrugated paper cartons.
(11) Inspect books for quality of treatment after allowing them to recover to room condition overnight.

Figure 2.88 presents a flow chart of the Wei T'o® system. After drying, books are placed in the process tank. The liquefied gas deacidification solution is pumped from the storage tank to the process tank. When the books are completely wetted, the excess solution surrounding the books is drained back into the storage tank for subsequent use. The pressure in the process tank is released and the books are damp-dried by the recovery

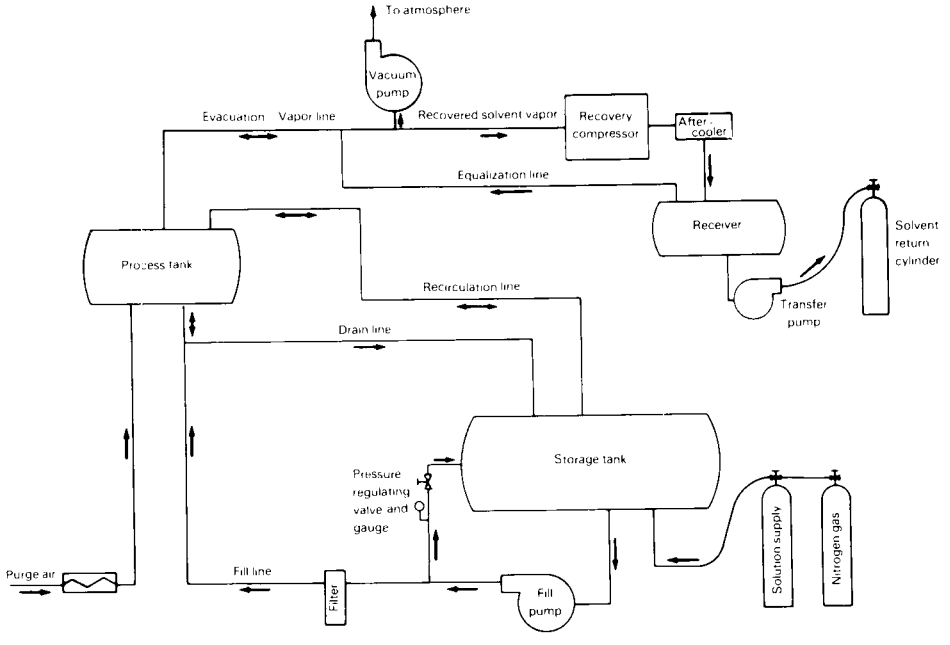


Figure 2.88 Diagram of Wei T'o® Non-aqueous Book Deacidification System.

compressor, whose output initiates the solvent recovery and condensation phase. The residual solvents are removed by the vacuum pump. This flash-drying process minimizes migration of the deacidification agent and deposits it throughout the books.

Figure 2.89 shows the arrangement of the components in the Wei T'o® system room. There are four main areas in this room:

(1) Quality control and testing;
(2) Preliminary treatments of warm air and vacuum drying;
(3) Non-aqueous deacidification; and
(4) Overnight recovery, conditioning and inspection.

The Wei T'o® non-aqueous book deacidification system is located on the ground floor of the Public Archives/National Library of Canada Building. The room has two doors. The liquefied gas deacidification solution is brought into the room in cylinders through the doors shown at the top of *Figure 2.89*. Books are selected and prepared for treatment just outside the door on the right side. Originally, the plan was to do everything inside this 30 – 40 ft (120m^2) room. Subsequently, a few tasks were moved outside to avoid crowding.

After receipt, the books are screened for their suitability for deacidification. Annotations with soluble ball-point inks and rubber-stamp identify marks are the primary cause of staining.

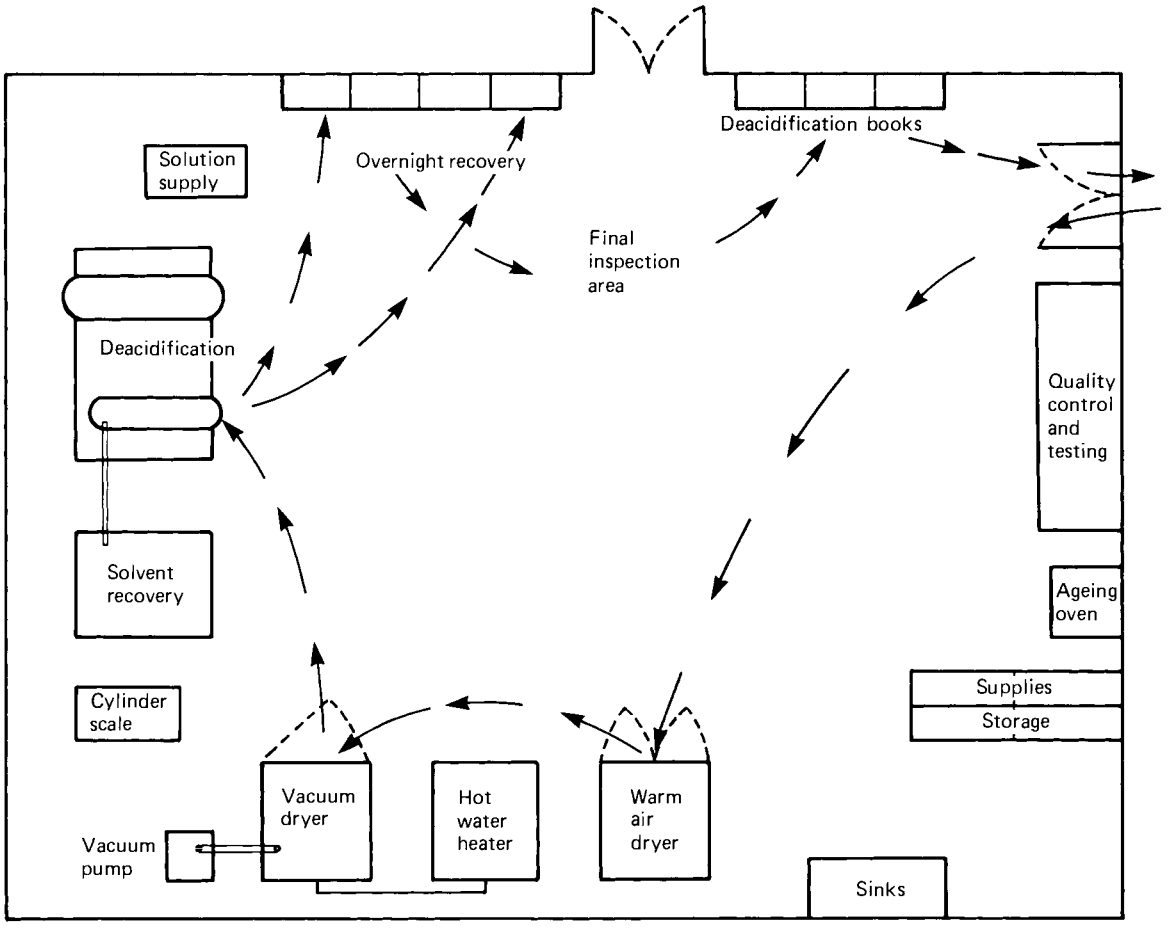


Figure 2.89

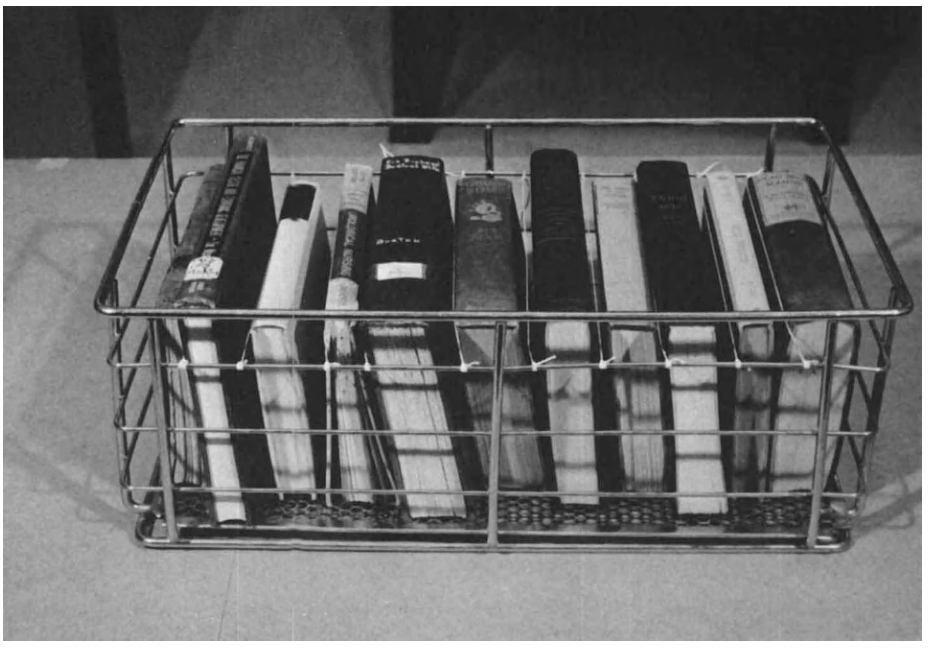
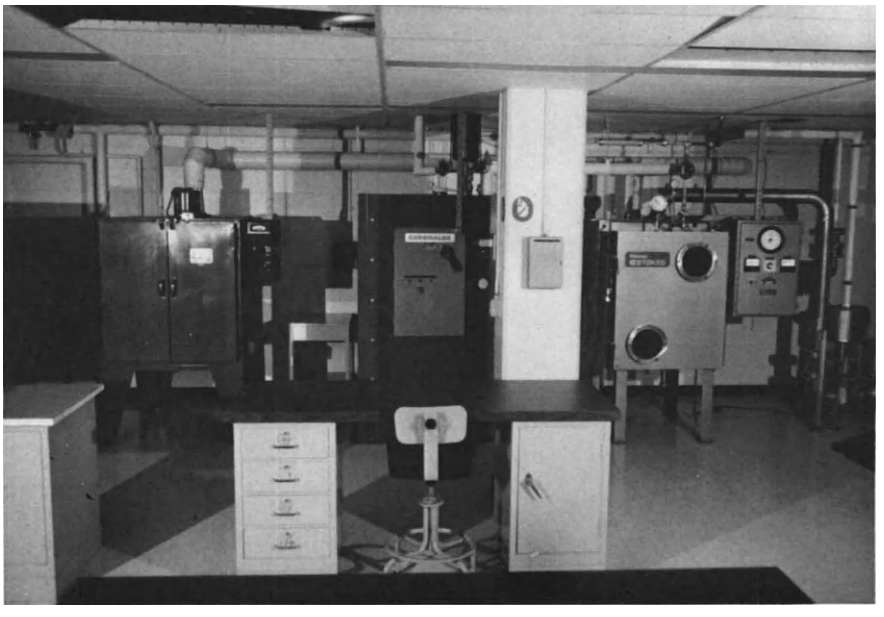


Figure 2.90 shows 12 books standing on their fore-edges and kept upright by cross-cords in a wire basket measuring 10 in. wide × 18 in. long × 7 in. deep (25 cm wide × 45 cm long × 17.5 cm deep). Many different book-loading schemes were evaluated before settling on the present spine down method (1981) using stainless steel wires, which hang from the support bars, as spacers and to hold thicker books slightly open.

Figure 2.91 shows the equipment used in the preliminary treatments. Starting from the left, we have (1) the Grieve warm air dryer and (2) the Chromalux constant temperature hot water heater for (3) the Stokes vacuum dryer.



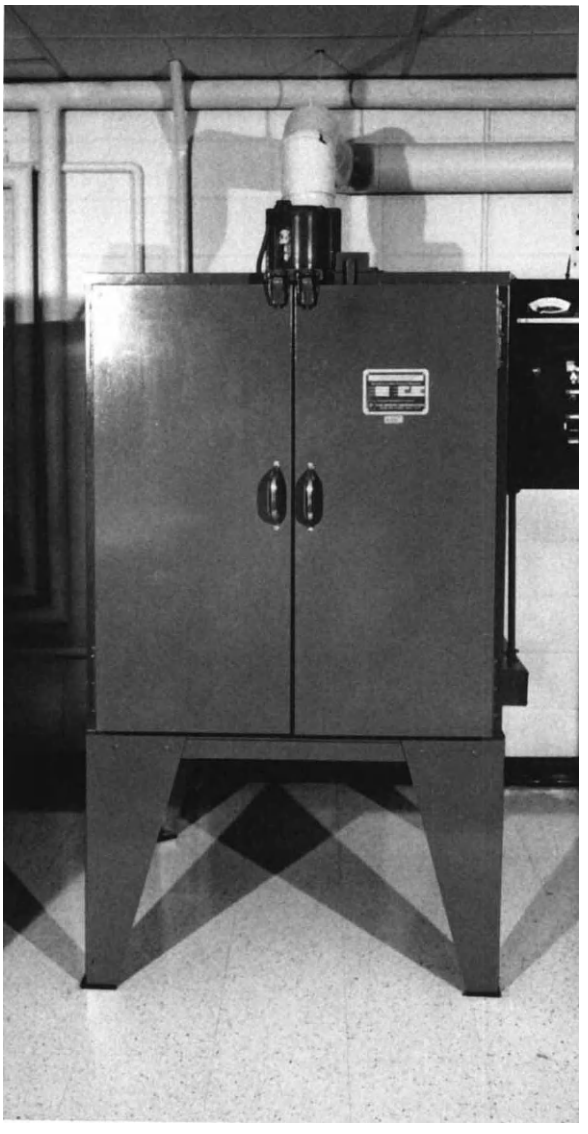


Figure 2.92 is a close-up view of the Grieve electrically heated, forced air dryer which operates at 140°F (60°C). The function of this dryer is to remove about 50% of the water in air-dry books. The dryer contains 18 baskets, six more than are deacidified in a normal day.

Figure 2.93 shows the interior of the Grieve warm air dryer. Air circulates from the fan at the top, down the sides, along the electric heaters at the bottom and up the centre. The amount of air leaving through the exhaust vent is controlled through the dampers of the inlets in the base.

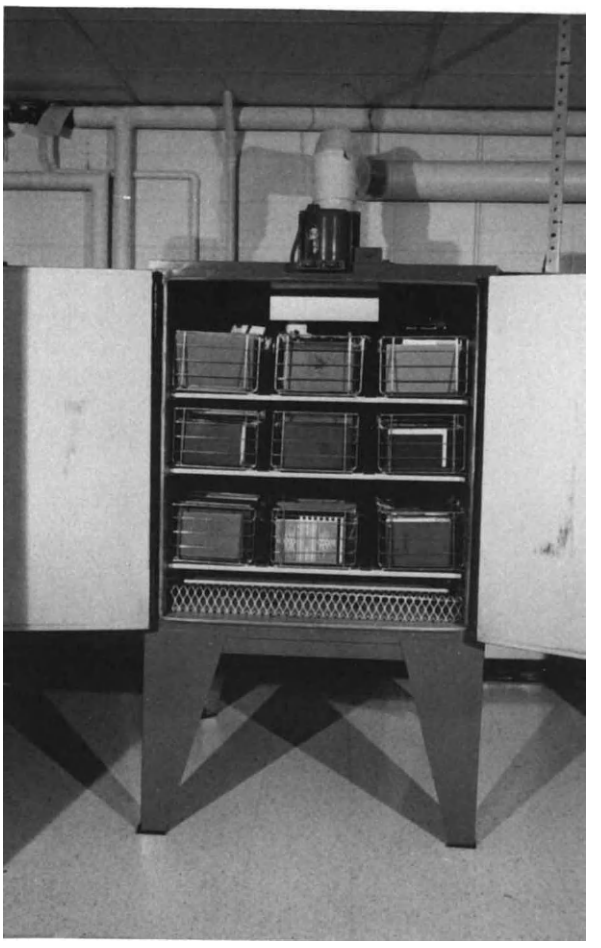


Figure 2.94 shows R. Couture, system operator, removing a basket of dried books from the Stokes vacuum drier. Twelve baskets of books are expected to be transferred into the vacuum dryer each evening and brought to a temperature of 140°F (66°C) and a high vacuum overnight. The paper in these vacuum-dried books is thoroughly dry. Contrary to conventional opinion, this bone-dry paper retains much of its strength and flexibility. The big book in the basket is the largest which can be deacidified by this pilot plant.

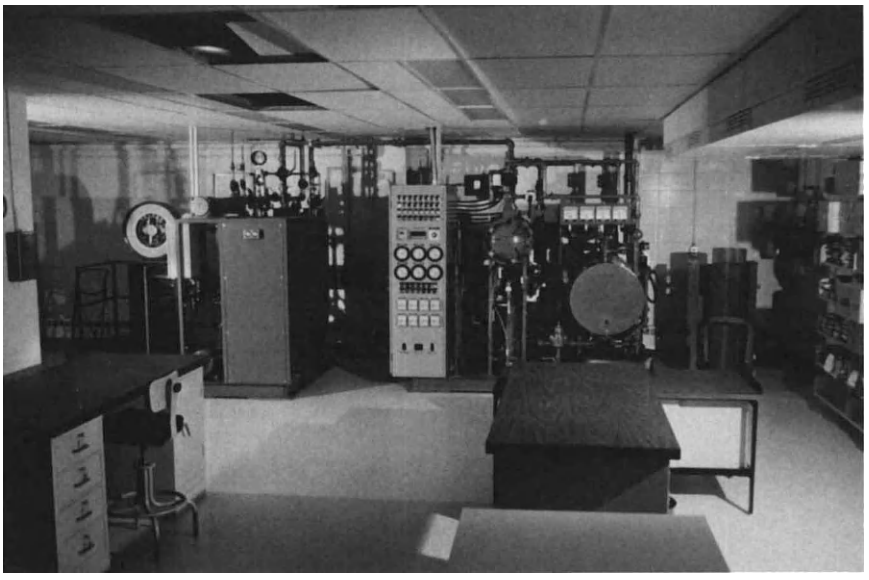
The external view of the Stokes vacuum dryer is presented at the right side of *Figure 2.91*. The control panel is shown at the middle right and the vacuum pump is at the bottom right. The two windows are used to observe drying books and to check shelf temperatures.

Figure 2.95 shows the deacidification area of the system room. Starting on the right side, there is a hydraulically operated cylinder inverter. The deacidification solution, supplied in 200-lb (91-kg) steel cylinders flows from the cylinder through flexible hoses into the storage tank. At the appropriate time, the deacidification solution is pumped from the horizontal storage tank at the right side to the process tank next to the control panel.

Two baskets of books are deacidified during each cycle in the process tank. The inside of the process tank measures 13 in. (30 cm) in diameter by 40 in. (100 cm) long. The typical treatment cycle takes approximately 1 hour.

The control panel shows the status of the system and the point where the process is in a cycle. The system controls are pre-set and a cycle, once started, proceeds automatically except for safety features and operator checks.

The recovery compressor is enclosed by a wooden box to minimize noise. The compressor recovers an estimated 80-90% of the solvent from the treated books. These solvent gases are cooled, condensed and stored in the recovery receiver tank behind the wooden box. The recovered solvent is used both to pressurize the process tank and for



recycling into new deacidification solution. Recovered solvent cylinders, placed on the scale, are filled with solvent from the recovery receiver for recycling at Wei T'o® Associates.

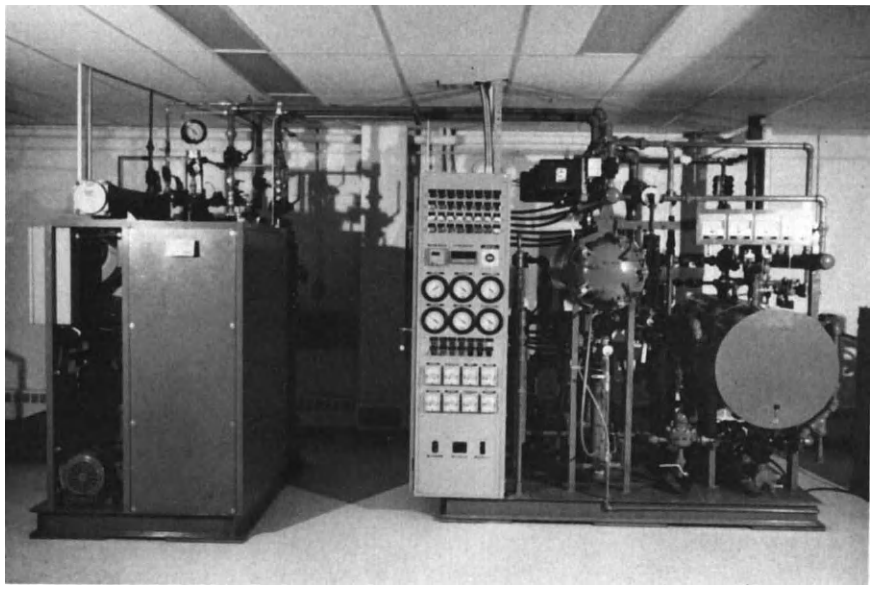


Figure 2.96 offers a closer view of the two main elements of the system: (1) the deacidification section (right) and (2) the recovery section (left). The main components of the deacidification section are the storage tank, process tank and control panel. The panel is approximately 2 ft wide × 7 ft tall (60 cm wide × 220 cm tall). The platform is about 5 ft deep × 8 ft long (150 cm deep × 240 cm long). Minor components include the temperature controllers, automatic valves, filters and pump.

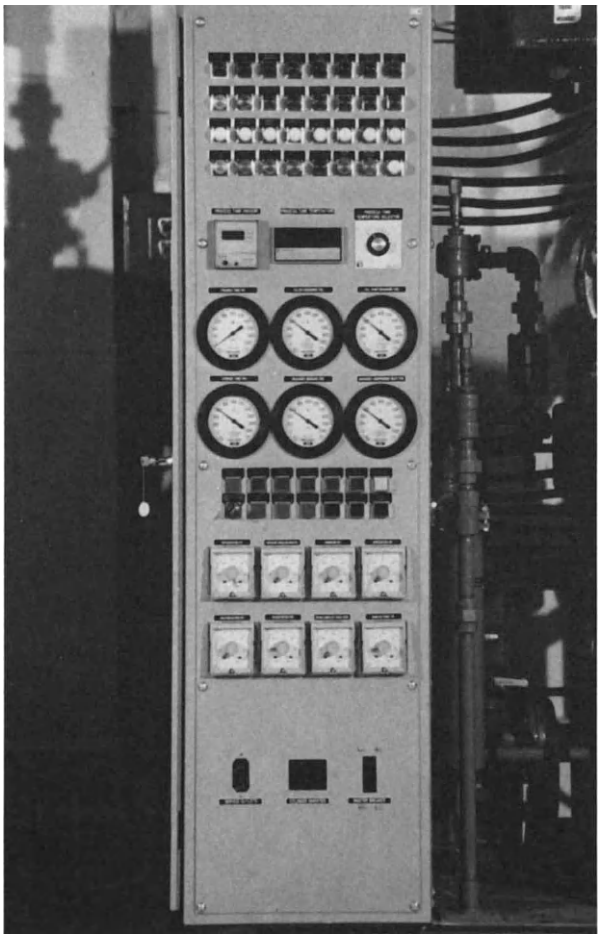


Figure 2.97 is a close-up of the control panel. The four rows of lights tell the operator what the system is doing. The lights tell whether there is enough solution, if the pressure is too high or too low, which components are functioning, where the system is in a process cycle and what the operator should attend to when an audible bell calls for his attention. The process tank vacuum pressure and temperature are indicated just above the pressure gauges. The pressure gauges give the pressure of the solution at six key points in the system. The press-button switches are colour coded and used by the operator to start and control each cycle. The eight timers are used to pre-select cycle times and vary cycles according to the nature of the books being treated. These timers can also be used, in combination with the press-button switches, to modify or terminate a cycle in process.

Figure 2.98 shows Couture closing the door of the process tank with a torque wrench. The use of a torque wrench provides part of the security necessary to ensure that the door is properly closed.

Figure 2.99 shows removing a basket of deacidified books from the process tank. Work is fast because these books are very cold, normally about −40°F (−105°C), to avoid moisture condensation. Temperatures as low as −221°F (−105°C) have been measured inside books with no observable harm to the books.

Figure 2.100 shows Couture sliding a basket of books inside a corrugated paper box before sealing it with pressure-sensitive plastic tape. The purpose of the box is to slow the rate at which books return to room conditions. This recovery inside a closed, but porous, box prevents the paper from becoming wet as it would in open air because the books are very cold at the end of the treatment. The moisture in air (73°F 55% RH), however, does pass through these corrugated kraft paper boxes as vapour and allows the books to gradually regain the moisture removed by vacuum drying.

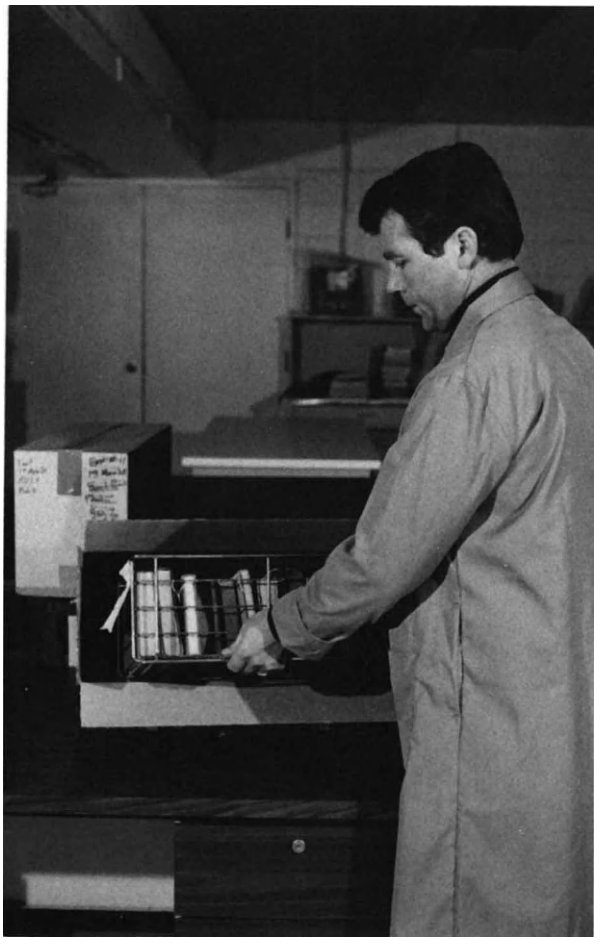


Figure 2.101 shows some of the books which were treated during the 1980 sequence of acceptance tests for the equipment. For acceptance, the system was required to perform ten sequential cycles without malfunctioning or showing signs of malfunctioning.

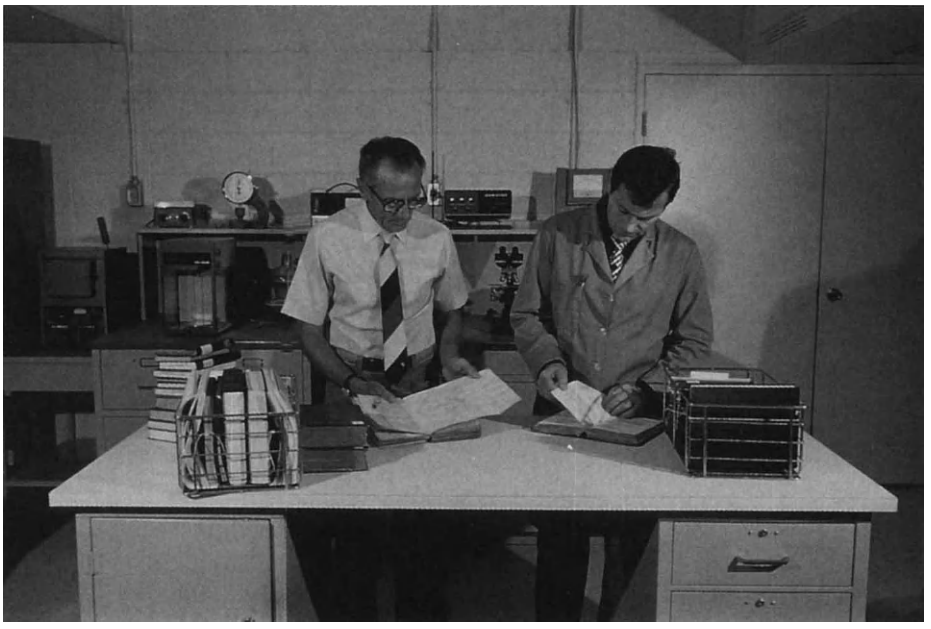


Figure 2.102 shows Pidek and Couture examining deacidified books after conditioning overnight. They are looking for staining, feathered inks, transfers from coloured plates or rubber-stamped identity inks, and any other physical or aesthetic defect the deacidification treatment may have caused.

Figure 2.103 shows equipment used in the quality control and test section to control the quality of procedures and materials used by the Records Conservation Department in this deacidification system.

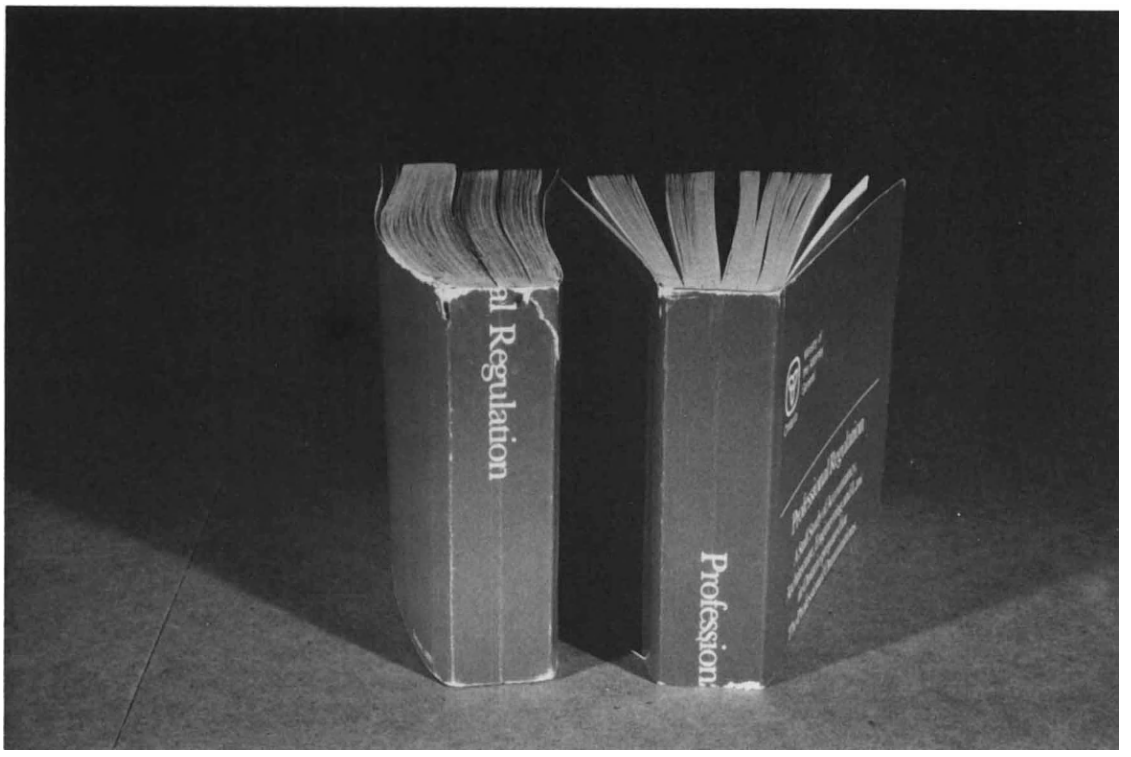
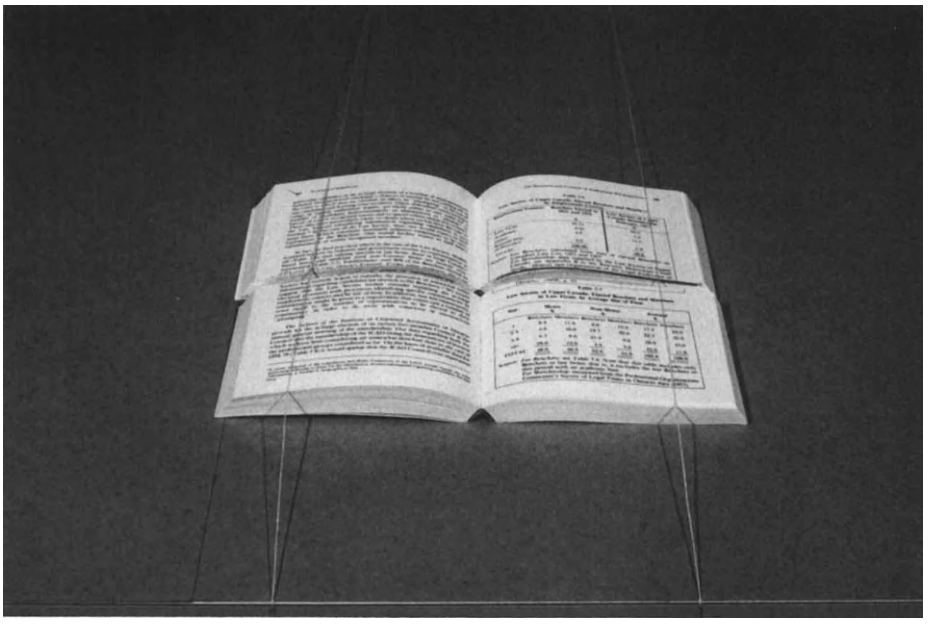


Figure 2.104 the deacidified half *(at right)* of an official Government of Canada publication against its untreated half. No differences are observable. Subsequent investigation (1982) indicates the treatment improves binding strength.

Figure 2.105 compares a deacidified page *(front)* from the same work *(Figure 2.104)* to its untreated half *(back)*. No differences are observable.



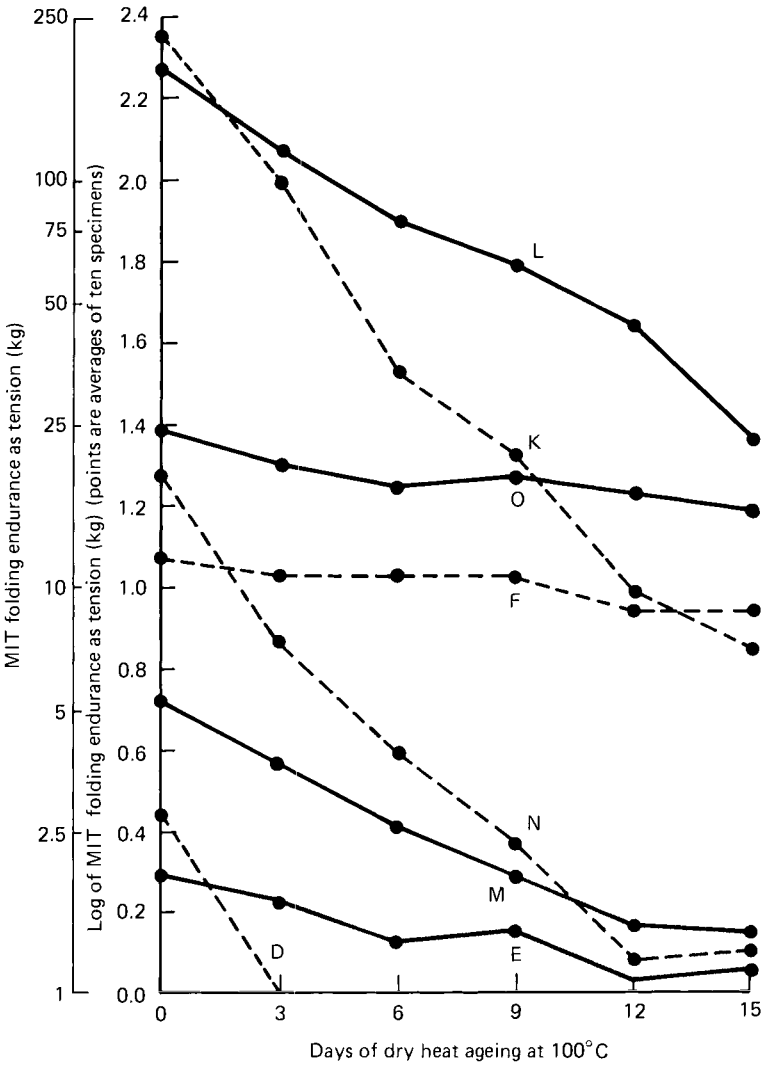


Figure 2.106. Accelerated Ageing Study of Strength Detention of Paper in Deacidification versus Untreated Books. In three cases the deacidified papers showed dramatic improvement over their untreated counterparts. In one case, a 1985 rag paper, no particular gain or loss was found.

Figure 2.106 presents the results obtained by ageing four sets of books treated in an early test cycle. All of these books came from a series and, though the papers in each set appear similar, they are undoubtedly not identical in each volume of a set. The D and E set is Volumes 16 and 15 from *The University Library,* Doubleday, New York, 1936. The books are unusual in that the highly nitrated cellulose nitrate coating on the book cloth was attacked and the paper in the untreated volume aged very rapidly. The F and G set is Volumes 2 and 3 from the *Life of George Washington,* Putnam, New York, 1860. This non-aqueous deacidification of stable rag papers appears to be non-harmful, since the deacidified paper remains about twice as strong as untreated papers. The K and L set demonstrates the benefit of deacidification to a still strong, chemical wood pulp paper. The M and N set is Volumes 1 and 2 from *King Edward VII* published in 1925 and 1927 by Macmillan in London. It is unlikely that the paper in both volumes is identical and, though an improvement is obvious, no conclusions can be drawn beyond the fact that a thick dense book with plates can be successfully treated. Subsequent improvements (1981) in the treatment cycle and in the formula of Wei T'o® liquefied gas deacidification solution have greatly reduced the problems of binding attack.

1982 Update

The article 'Mass deacidification at the NL (National Library of Canada),' *National Library News,* 14, 1-3, March-April (1982), summarized the system and closed by stating:

> The system is designed to accommodate 5000 books per week, based on 24-hour-a-day, seven-day-a-week operation.
>
> The National Library is fortunate to have this outstanding system available for the treatment of its collections. The Wei T'o mass deacidification system at the national

Library/Public Archives appears to be a major breakthough in book preservation. With it many more books than before will be able to undergo deacidification. Savings in money and time over the traditional methods of deacidifying books are impressive. The time involved in treating books by the manual method can be eliminated, so that the cost of treating each book can be reduced to about $3 or $4 from approximately $150. Moreover, because more books can be treated for preservation, replacement costs are cut as well.'

Sources of Further Information

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Smith, R. D., (1979). 'Preservation: library need and industry opportunity: Part 1,' *Library Scene,* 8, December, 10-13.

Smith, R. D., (1980), 'Preservation: library need and industry opportunity: Part 2,' *Library Scene,* 9, March, 10-12, 14.

Smith, R. D., (1982). *Treatment of Cellulosic Materials,* US Patent No. 4,318,963, Washington, DC: US Patent Office, 9 March.

Note

1 Wei T'o, an ancient Chinese god, protects books against destruction from fire, worms and insects, and robbers, big and small.

Acknowledgements

The author is grateful to the Public Archives of Canada for its encouragement and support of this work, and for permission to take these photographs and present this report.

2.4

Mounting and Storage of Art on Paper

2.4.1 The mounting and storage of prints, drawings and watercolours at the British Museum

Eric Harding

A discussion of the storage problems and mounting (matting) procedures used at the British Museum is presented. The system of mounting fulfils:

(1) Aesthetic requirements (allowing for greater visibility of the work of art);
(2) Conservation standards (physical protection, acid-free materials);
(3) Basic security needs;
(4) Maximum use of limited storage space.

Mounting (matting) is carried out to fit definite storage conditions which determine both board thickness and mount sizes, which are standardized.

A detailed description of inlaying (false margin) and a method of sandwiching recto/verso compositions between sheets of Perspex (poly(methylmethacrylate)) is described.

Conservation materials used are listed.

Storage of the British Museum's collection of drawings and watercolours is basically met in two ways, mounted and unmounted. The system means that the Print Room, (or 'Student's Room'), can accommodate large numbers of portfolios for the loose material in addition to the Solander boxes containing the mounted material. The mounting is carried out to conform to definite storage conditions. The actual storage area consists of the Print Room in its entirety and the mezzanine floor below the Print Room. This is an area the size of the Print Room with offices for curatorial staff and rows of cupboards and cases for storage. Even the curatorial offices are storage areas. Despite this apparently ample space the department is now, and has been for a very long time, desperately short of storage room. Every cupboard and portfolio is full. This situation is so critical that to add even one additional Solander box of mounted drawings to the collection often means that several full-length cases have to be rearranged.

The collections that make up the nucleus of the Print Room Collection — the Sloane, Fawkener, Crackerode and Payne Knight — were originally in albums. The earliest method of separate mounting, which dates from the first half of the nineteenth century, was to edge the print or drawing onto thin card with no top mount. This solution fulfilled the requirements of security but did little for the protection of the object. The method was to paste an area of about 3 mm wide along the four verso outside edges, position the drawing onto a piece of card, and then place it under pressure to complete the process, usually in a screw press. Despite the obvious inadequacies of this system, it served to keep the material separated and, with careful handling, in fairly good order. There were exceptions, notably in the edging down of the watercolours of the Turner Bequest, mostly the 'colour beginnings', where problems have arisen. Because of the nature of the paper and the manner in which it was mounted, quite severe cockling has occurred, principally due to the fact that the drawings were insufficiently relaxed with applied moisture prior to being laid down onto the boards. Absorption of moisture from the atmosphere causes the paper to expand, and, as it is constricted on all four sides, it has to undulate in the centre. Fortunately very little real damage has occurred as a

result of this method and the drawings can be straightened out by relaxation with applied moisture.

The magnitude of the British Museum collection means that regular inspections are necessary. Loose prints housed in portfolios are further protected by folders of acid-free paper which is renewed from time to time as it becomes worn. From a practical point of view, this method is preferable to interleaving with acid-free tissue, which is frail and easily mishandled. Portfolios are of the standard type made from thick millboard lined with acid-free rag paper. There are linen covers on the inside for extra protection.

The Solander boxes which house practically all of the mounted drawings are of very rigid wooden construction, lined with acid-free rag paper and on the outside covered with buckram and with leather spines. The fasteners are mostly of the press-stud type (as opposed to hooks). The boxes are extremely well made and durable and many even date back to the origins of the Print Room. The Solander boxes are mostly stored horizontally, which is the best method for drawings.

Upright storage encourages the undesirable free movement of the mounted material in all but the most tightly packed boxes, and with it, the likelihood of pigment disturbance. The main advantages of horizontal 'stacking' are that the mounted drawings tend to remain flat under their own weight, and with no movement.

Temperature and humidity levels in the Print Room are generally satisfactory in the period spring to autumn, maintaining 52% RH ± 5% and 18°C ± 4°. This variation has a minimal effect on the collection as a whole in view of the enormous amount of wood, glass and paper buffering present. (i.e. storage cases and mounting materials).

During the winter, convected warm air from radiators causes large variations in humidity from hour to hour and place to place in this very long high room (Print Room), and many serious problems arise from the fact that the storage cupboards become heated from behind. Proposals to fill all cavities with thermal insulation are expected to bring about considerable improvement. There is unfortunately no prospect at present to extend full air-conditioning from the Prints and Drawings exhibition gallery to the Print Room and mezzanine floor below.

There are four standard sizes for the mounted material, namely 22 in. × 16 in. Royal, 27 in. × 20 in. Imperial, 32 in. × 24 in. Atlas and 45 in. × 29¾ in. Antiquarian or Double Elephant. Most of the material is mounted in the size 22 in. × 16 in. Royal. Some would recognize this size, more correctly, as half-imperial. The standardization of mount sizes in museums in the UK generally would be difficult in view of the vast amount of material already mounted in set sizes. Mounting methods also vary considerably. Many still favour the method whereby the edge of the drawing is overlapped by anything up to 6 mm by the top cut-out window or aperture mount/mat. This method has obvious disadvantages; for example, it must cover part of the original surface of the paper and sometimes even the image. In display, such mounting methods cause differential fading, which, on remounting to show the object in its entirety, becomes very unsightly. This kind of damage is impossible to rectify. For mounting (or matting) many favour thick board for maximum rigidity and protection, but this requires adequate shelf space.

Whilst recognizing the ideal, modifications are necessary, and therefore in view of the serious shortage of space we are obliged wherever possible to reduce the total thickness of the mount or mat. One useful development in the mounting of prints has been the use of single-ply mounting board for top mount and back board. The print is hinged or 'tabbed' onto the back board of a mount with thin Japanese paper *(kozo-shi)* using gluten-free wheat starch paste[1] or Cellofas 'B' Grade 3500 Granular[2]. After making, the Japanese gluten-free wheat starch paste is stored in water, in 2-litre stone jars with 10 ml Paraformaldehyde added as a biocide. Cellofas 'B' is used at 2% strength, can be made up in very small quantities and needs no biocide. After the print is affixed into position it is covered with Melinex[3] (Mylar) (poly (ethylene terephthalate)) sheeting 75 μ thick. This enables the aperture in the top mount to be cut so the whole of the print is showing. At the moment mounting board[4] made in the USA is used, but some manufacturing of acid-free rag fibre board is expected soon in the UK. Our range consists of 1 to 5 ply, i.e. 1 ply (500 μ), 2 ply (1000 μ), 3 ply (1500 μ), 4 ply (2000 μ), 5 ply (2500 μ). For drawings we are now using 3-ply as standard. An exception would still be a chalk or pastel drawing which would be given a 5-ply top mount for additional protection. In practically every case the drawing is given an inlay or false margin of acid-free paper which enables it to be handled more easily and attached safely to the back board of the mount. To make an inlay a piece of acid-free paper is required of roughly the same strength and weight as the original drawing and about 35 mm larger all round. The drawing is placed in the middle and the four corners marked. Then the centre of the paper is cut out 3 mm inside the four corners or marks and the inside edge of the aperture in the paper is then chamfered down with a surgical scalpel or similar

tool so that when the drawing is attached there will be no ridge. The drawing is then turned face down and the cut-out centre piece of acid-free paper placed over the verso, which will leave a margin for pasting i.e. 3 mm all round. The adhesive is applied and the cut-out centre discarded. The drawing is then laid onto the inlay using the four corner marks as a guide. The ensemble is then placed between two sheets of fine Japanese tissue with additional blotting paper either side and then between pressing boards and into a screw press with very gentle pressure, the handle being turned slowly until the first signs of resistance are felt. If the adhesive has been applied carefully, both tissue and blotting paper can be removed cleanly when dry, which is usually about twelve hours later. If in doubt one should use silicone release paper on the underside instead of Japanese tissue. However, this method sometimes extends the drying time. When dry, the inlay paper and the drawing form a single sheet which can be affixed to the back board by applying adhesive or hinges to the top of the inlay.

The mount can be hinged full-length to open-book fashion, or can have adhesive applied around the four outer edges about 6 mm or so to form a solid mount. This method provides extra rigidity, and is also useful from the security aspect. Drawings with images or inscriptions on the verso which extend to the edge of the paper, and which cannot therefore be inlaid are usually sandwiched between two pieces of 1 mm thick poly(methylmethacrylate), better known by its trade name of Perspex [5] or Pexiglas. The Perspex is first treated with anti-static polish before the sealing operation which is done with acrylic pressure-sensitive tape. The 'sandwich' is then enclosed in a centre mount or mat, flush with the surface, and top and bottom mounts are fixed afterwards. Positioning of the drawing within the sandwich is effected by slips of silk which are attached with Cellofas 'B' or gluten-free starch paste to the drawing, and by Texicryl 13-002, [6] an acrylic emulsion, to the Perspex. The final process in mounting a print or drawing is to round off the corners and edges of the mount with a pad of glasspaper. We have found that enormous, and sometimes irreparable, damage can be caused to an object by the careless handling of another mount in the same box, when pointed corners are accidentally dragged across the drawing or print below. This is especially so in the case of mezzotints, which are visibly damaged in the darker areas from even gentle abrasion or contact.

Every print and drawing newly acquired has to be stamped with a register number and sometimes also a particular collection stamp. This is done with an engraved brass tool and ordinary carbon-pigmented oil-based printing ink. It has been found that this fulfils all the departmental security needs in that it is a permanent method of marking the object. The only way of removing this ink once dry is by a mechanical scraping or abrading operation which, of course, would also damage the paper surface and be readily seen. It will also withstand almost any aqueous or solvent treatment without disturbance. Hence it will withstand any conservation treatments. The mount itself is also stamped with the register number and collection stamp (if any), the artist's name, and abbreviated references to any standard catalogues.

This is, of course, an element of skill and touch in application as with everything. For example, too much pressure may result in too deep a penetration, especially on thin paper. A shaky hand would mean smudging of the collection stamp or registration number. However, if a mistake of this sort occurs the ink can be safely and easily removed with suitable solvents providing this is done before drying out occurs.

Thus the prints, drawings and watercolours in the collection can be mounted neatly and safely, and stored well enough in very full and crowded accommodation.

Acknowledgements

The author thanks Dr. M. W. Pascoe, Keeper, Department of Conservation and Technical Services for his advice in the preparation of this article and for permission to publish, and to J. A. Gere, Keeper, Department of Prints and Drawings.

Notes and References

1. Japanese Wheat Starch paste: Mayuyama & Co. Ltd., 11-2 Chome, Kyobashi, Chuo-Ku, Tokyo, Japan.
2. Cellofas 'B' Grade 3500 Granular (sodium carboxymethyl cellulose), Picreator Enterprises, 44 Park View Gardens, London NW4 2PN, England.
3. Melinex, manufactured by ICI Ltd.
4. Andrews, Nelson and Whitehead Mounting Board obtainable in UK from: Lawrence & Aitken Ltd., Albion Works, Kimberley Road, London NW6 7LS, England.
   Rising Paper Company Mounting Board obtainable in UK from: Universal Fine Arts Board & Display Co. Ltd, 95a Marylebone High Street, London W1M 3DD, England.
   Conservation Resources International Mounting Board, obtainable in UK from

Conservation Resources (UK) Ltd., Unit One, Littleworth Industrial Estate, Wheatley, Oxon OX9 1TZ, England.

5. Perspex (poly(methylmethacrylate)) manufactured by ICI Ltd.
6. Texicryl 13-002 acrylic emulsion manufactured by Scott Bader & Co. Ltd., Wollaston, Wellingborough, Northants NN9 7RL, England.

2.4.2 The mounting and storage of the graphic arts collection at the National Gallery of Canada

Peter Zegers

The NGC houses the major collection of prints, drawings and photographs in Canada. As a truly national institution meant to serve the country from coast to coast, the NGC constantly generates from its graphic arts collection exhibitions which travel across Canada. Moreover, the NGC is called upon by numerous small Canadian institutions to provide loans for exhibitions. These loans often constitute more than 50% of the works included in the exhibitions of the borrowing institutions.

The constant demand on the graphic arts collection led to the development of special mounts for prints and drawings. The standard back board and window board mount is provided with an additional protective handling front composed of Mylar 'sandwiched' between two pieces of acid-free board. The benefits of this front are twofold: constant handling of the works does not soil the standard mounts, thus reducing expenses in the long run; and the Mylar window allows quick identification of prints and drawings, thus eliminating the danger of abrasion that is poised by the removal of interleafing tissue. The drawbacks of this front are the dust-attracting qualities of Mylar, the added thickness of the mounts and the increased initial cost.

A system of mounting large works of art on paper also has been developed. Oversize prints with margins are supplied with corner supports made from folded paper or linen and, in other instances, the hinges are pulled through a fluted plastic backing support. Because the oversize works of art cannot be stored in Solander boxes on shelves, they are permanently framed and stored on sliding shelves, one framed work per shelf.

The prints and drawings in the graphic arts collection[1] of the National Gallery of Canada are mounted in four standard sizes[2]. Once mounted, the works are stored in Solander boxes, which are made to conform to these four sizes. When the works are exhibited they are placed in frames constructed to fit the various sizes and are shipped, still framed, in slotted crates which are built to serve the four size system. Oversize works, which require special mounts, or no mounts at all, are kept permanently framed for safe handling and storage.

Mounts

The standard mount consists of a back board and a window board. To this standard mount is added a protective handling front composed of a sheet of Mylar[3] 'sandwiched' between the two pieces of window board. The size of the sheet of Mylar varies with each of the four sizes. In each case it is 1 in. smaller than the size of the mounting board. This allows double-sided adhesive tape[4] to be used to secure both the Mylar to the boards and the boards to one another *(Figure 2.107)*.

The protective front is attached to the back board with gummed linen tape[5]. A ¼ in. space between the front and the back board is provided in order to allow the protective front either to cover the window board or to swing behind the back board.

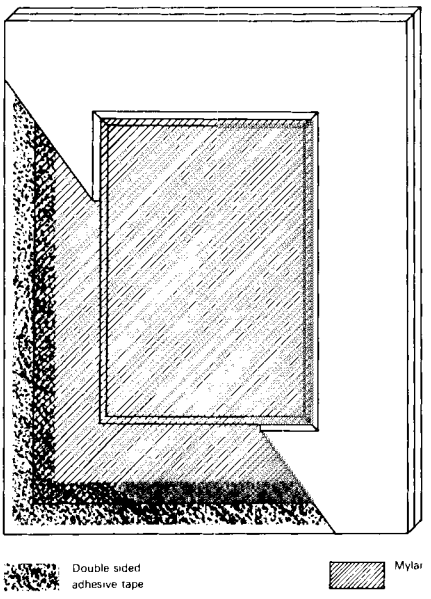


Figure 2.107.

The latter is necessary when the work is to be framed *(Figure 2.108).*

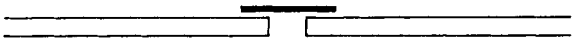


Figure 2.108.

The window board is hinged to the top of the back board with another gummed linen tape *(Figure 2.109).*

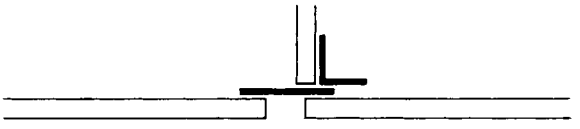


Figure 2.109.

Window openings in the case of prints with margins, are determined relative to the platemark, or, in the case of drawings, by the limits of the composition. In the first instance the margins are partially covered by the window board. If the entire support is to be considered an integral part of the composition, the window opening is made slightly larger than the size of the sheet — that is, the works are 'floated' *(Figure 2.110).*

Sometimes there are works in the collection which have been laid down on heavy, thick secondary supports. If they are to remain on these supports, which create a problem because of their weight, it is necessary to find a safe way of mounting

Figure 2.110.

them. The solution to this problem is the use of 'sunken' or 'support' mounts.

An opening corresponding exactly to the dimensions of the work is cut into a piece of mounting board of the same thickness of the work. Then this board is attached to the backing thus creating a 'sunken' mount into which the work snugly fits. A standard window mount and a protective front are then attached as is usual. This method of mounting secures the work and prevents it from sliding if the hinges give way *(Figure 2.111).*

Figure 2.111.

Hingeing

To secure the works to the back board conventional methods of folded and T-hinges are used. These hinges, depending on the dimensions and condition of the work, are either made from Japanese paper and affixed with wheat or rice starch paste, or made from gummed linen tape. Works on a heavy support or on a secondary support are hinged and further secured with corner pieces made of folded acid-free paper or gummed linen tape. Hinges sometimes are eliminated and folded paper or linen corners, securing the works at all four corners, are substituted *(Figure 2.112).*

Figure 2.112.

Works that cannot be fitted into the standard size mounts are designated as oversize and are permanently framed. If the oversize works are smaller than the sheet of mounting board produced by the manufacturer[6], the mounting board is used as the support. If the oversize works are larger than the manufactured sheets of mounting board, an alternative support made of fluted plastic[7] and acid-free paper[8] is used.

A contemporary work of art often poses a special problem because of its large size. To maintain the pristine condition of its support and surface such a work is framed immediately upon entering the collection. First, the work is laid upon a sheet of fluted plastic, the front of which has been covered with acid-free paper. This paper, affixed to the fluted plastic support by means of linen tape, serves as a buffer between the work and the fluted plastic support. Then the work is joined to this buffered support by means of a series of hinges, the number of hinges being determined by the weight and dimensions of the work. These hinges, however, are not affixed to the buffered front of the support; rather they are pulled through slits cut in the support and are folded down and secured by means of tape[9] to the back of the fluted plastic. This method of hingeing has been proved to minimize the danger of hinges giving way under the weight of the work *(Figure 2.113)*.

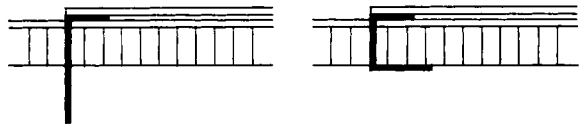


Figure 2.113.

Frames

A four-membered hardwood frame is favoured, both for the framing of works of standard sizes and for the framing of oversize works. This type of frame combines attractiveness and usefulness. The frame also is used for posters which have been mounted onto unbleached cotton and put on a stretcher. Works without a mount — especially the large contemporary works — are separated from the glass or Plexiglas by spacers made of plastic or sealed wood *(Figure 2.114)*.

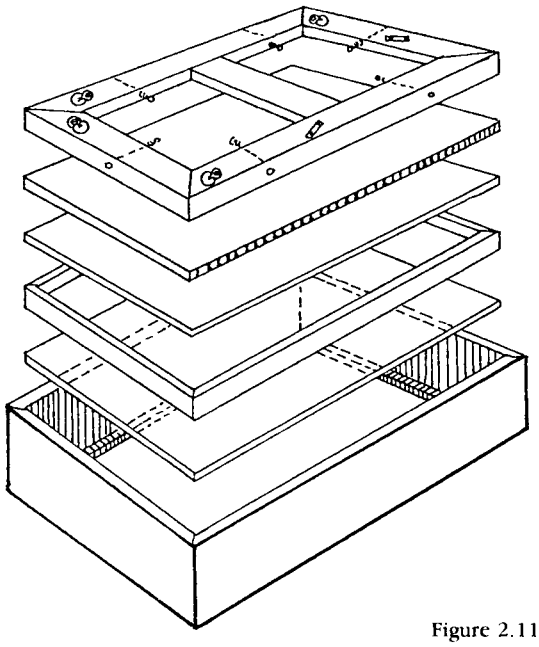


Figure 2.114.

An alternative to the four-membered hardwood frame is the Plexiglas shell or box. The latter is sometimes favoured in order to direct attention to the work with a minimum of distracting framing elements *(Figure 2.115)*.

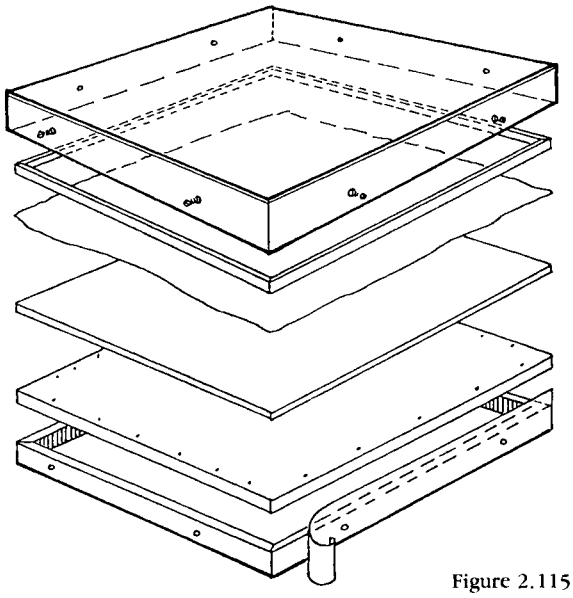


Figure 2.115.

Storage

The collection of graphic art of the NGC is housed in an environmentally controlled storage vault. A Halon 1301 gas system[10] protects the collection from fire. Modular storage units contain the works which are stored in Solander boxes or in frames.

Storage — Solander boxes

An average of ten mounted works are stored in each Solander box. The Solander boxes are stored, one box on a shelf, in shelving units that are designed as components of a modular system. This modular system is based on three types of shelving units:

Type one: a unit of 20 fixed shelves that is designed to hold 20 boxes either of size 1 or of size 2;
Type two: a unit divided into three compartments, each of which contains ten sliding shelves that is designed to hold a total of 30 boxes of size 3;
Type three: a unit divided into two compartments, each of which contains ten sliding shelves, that is designed to hold a total of twenty boxes of size 4 *(Figure 2.116)*.

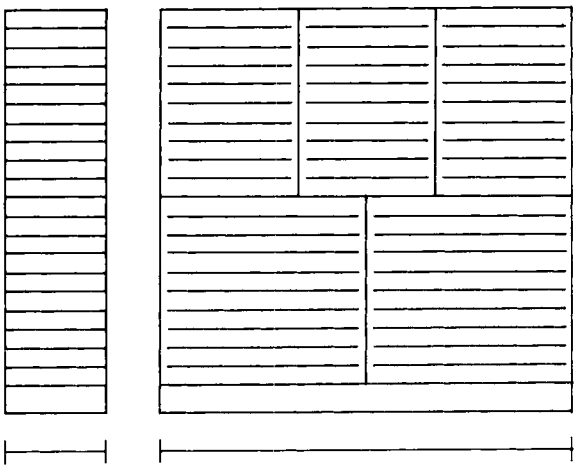


Figure 2.116

A 'basic' storage unit is built using these three types of shelving units. First two shelving units of Type three are placed back to back. Units of Type three are always placed nearest to the floor to make for easier handling of the large and heavy boxes of the size 4 that are shelved in these units. The two units of Type two are placed back to back on top of the Type three units. Finally three shelving units of Type one are placed with their backs to each end of the rectangle that has been formed by the other units. The result is a rectangle with shelving on all four sides *(Figure 2.117)*.

This basic storage unit comprises shelving for 220 boxes; 120 boxes of size 1 and/or 2; 60 boxes of size 3; and 40 boxes of size 4. The unit occupies a total floor space of 3.40 × 1.59 cm (5.40m^2).

Storage — framed works

Oversize framed works are divided into two categories:—

(1) Oversize works mounted on the largest size available commercial mounting board, and
(2) Oversize works larger than the largest size of commercial mounting board.

In the first case the works are shelved; in the latter CASE the works are too large for shelving and are hung on sliding racks in the same fashion as are paintings.

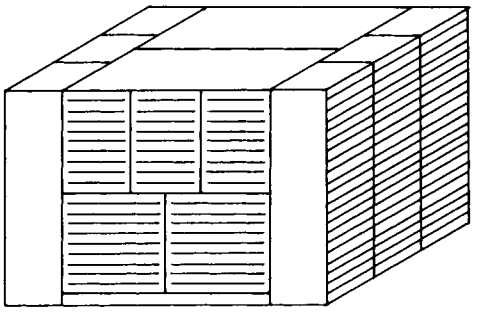


Figure 2.117

The cabinet for oversize framed works contains 30 sliding shelves. One oversized framed work, with or without a mount, is stored on each shelf. As is the case with the mounted works stored in Solander boxes, flat storage is preferred. Individual shelving of framed works reduces the danger of damage that might occur to the wooden frame and the glass or Plexiglas. Given the expenses involved in proper care, in mounting and in framing, this aspect is an important consideration in promoting individual storage space. An additional advantage of this shelving is that it may be used for storage of oversize portfolios *(Figure 2.118)*.

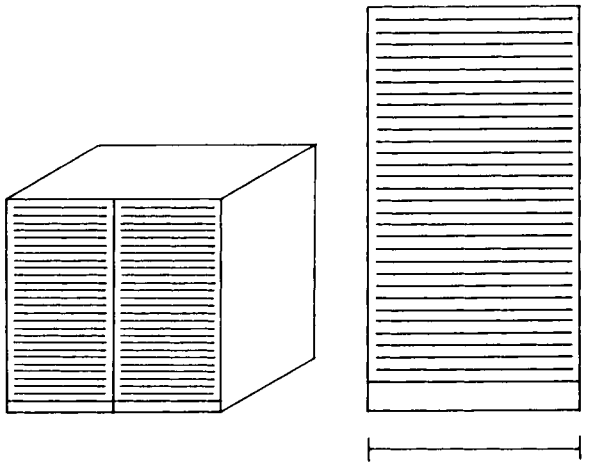


Figure 2.118

Notes and References

1. Collection of about 10 000 original prints and drawings, both Canadian and non-Canadian. The Canadian collection contains works by artists from the mid-eighteenth century to the present. The non-Canadian collection primarily represents artists of the major European artistic centres, from the fifteenth to the twentieth century, and American artists of the nineteenth and twentieth centuries. All major techniques and media of prints and drawings are represented.

   Collection of about 9000 photographs (positive prints made from silver and other metallic salts, as well as various pigment and ink processes) concerned with the history of photography as an image-making process. The collection spans the period from about 1835, the earliest days of photography, to the present. International in scope, the collection includes the work of well-known photographers
2. Standard sizes are: Size One: 18 in. × 14 in.; Size Two: 21½ in. × 16 in.; Size Three: 28 in. × 22 in.; Size Four: 28 in. × 36 in.
3. Mylar is recommended because no plasticizers or other harmful additives are present in it. The thickness recommended is .05 millimetre.
4. A 3M product No. 465. It is a 2 in. wide linerless double-sided adhesive tape.
5. Gummed cloth tape.
6. A 36 in. – 44 in. acid-free, neutral, all rag mounting board of high quality, made expressly to National Gallery of Canada specifications.
7. Fluted plastic backing sheets are composed of 90% polypropylene and 10% polyethylene.
8. An acid-free, all-rag, neutral isolating and mounting paper of high quality, made expressly to National Gallery of Canada specifications. It comes in rolls 76 in. wide.
9. A 3M product No. 810. Any adhesive tape which adheres to the fluted plastic surface will suffice.
10. Halon 1301 (bromotrifluormethane Br CF3) is a colourless, electrically non-conductive gas that is an effective medium for extinguishing fires. Since it is a 'clean' fire-extinguishing agent, it leaves no residue and is thus much safer to use where valuable material is being stored.

2.5
Leaf-casting

2.5.1 Notes on the early development of leaf-casting

Esther Boyd Alkalay

The first experiments in leaf-casting as a mechanical method of infilling missing areas in damaged papers were carried out by Yulia Petrovna Nyuksha in the Saltykov-Schedrin Library in Leningrad in the late 1950s. Inspired by her work from 1961 on the author constructed a series of leaf-casting machines and installed a number of systems, initially in Sofia, Bulgaria and then, after 1969, in Israel. The improved models produced there have been acquired by a number of institutions in Europe and the Americas. Historical notes are here given of these developments and the influences of this work on the manufacture of leaf-casting equipment and its operation by others.

It is impossible to talk about leaf-casting without mentioning the previous generation of restorers who employed suspensions of paper fibres for filling the missing parts using spoons. When I took the first steps in the field of restoration, I corresponded with two of the pioneers of this method — Ladislaw Zedletsky and Joseph Wizkotchil, both from the National Library of Prague. I also tried to work in this way and I think that this slow and laborious method paved the way to mechanical leaf-casting.

The first experiments on leaf-casting as a mechanical method of conservation and restoration were carried out by Yulia Petrovna Nyuksha in the Library Saltykov-Shchedrin in Leningrad, at the end of the 1950s. Her ideas were developed in various ways and with diverse modifications in different places, using both hand — and electrically operated machines, which generally produce the same effect.

Inspired by Nyuksha's article (in *Disinfection and Restoration of Library Materials,* Leningrad, 1959), I constructed my first machine before visiting Leningrad. I carried out the experiments with a cylindrical leaf-casting apparatus (sheet forming) which was used for preparing samples in the laboratory of a paper mill in Sofia. When I had achieved satisfactory results, I received encouragement and financial support from the National Library in Sofia, where I established the laboratory for restoration in 1956. Later, in 1963, when I visited Leningrad for the first time, to participate in the international meeting of conservationists, I saw Mrs Nyuksha and her small leaf-casting machine. It was square and of the same type as used in the laboratories of paper mills for testing pulp *(Figures 2.119* and *2.120).*

My first machine had a working surface of 48 cm × 65 cm and was equipped with a mechanical water pump. The perforated plates were arranged in a primitive way. Natural silk was used in the beginning as a supporting screen, which left marks on the paper after it had been dried and pressed in a drying apparatus, as used by photographers. The paper fibres were obtained from a paper mill and PVA was used as adhesive.

In Sofia I built another two machines of the same type, but with slightly larger surfaces; one for the Party archives and the other for the archives of the Academy of Sciences *(Figure 2.121).* As far as I know, one of them is now in the restoration department of the Library Lenin in Moscow.

In 1965 I started to construct a leaf casting machine and system, complete with Hollander

Figure 2.119

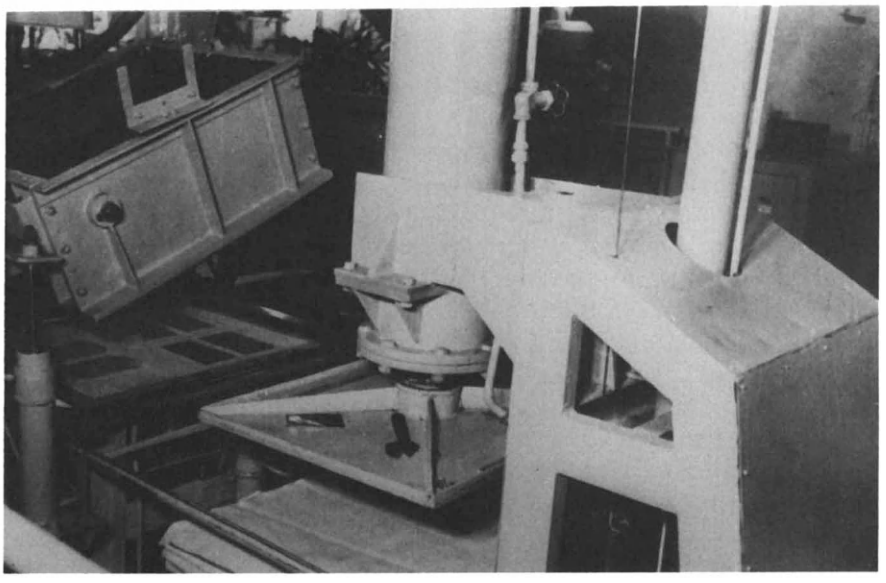


Figure 2.120

beater, hydraulic press, two drying presses and an improved leaf-casting part *(Figure 2.122)*. The working surface was about 50 cm × 70 cm. There was a water pump, perforated plates and a water supply, all arranged more conveniently. I used mobile moulds, which were moved by hand on rails. The leaves were arranged for casting on the right and were transferred from the machine to the press on the left. This machine was bought by the Army Archives.

In 1967 I participated in the IADA conference, which took place in Freiburg, Basel and Zurich. Because of my difficulties with the German language, I had contact only with Joseph Ries from the Stadt-Archiv in Zurich and later with Trobas from Graz, to whom I showed my work and explained the principles of leaf-casting. Only a few months later, Joseph Ries visited me in Sofia and saw my first machine. Through an article which I wrote for IADA and through Joseph Ries the idea of leaf-casting was publicized in West Germany and Austria, and soon there were simple variants of hand-operated machines in many libraries, archives and workshops of private restorers in these two countries.

Unfortunately, I have no up-to-date information about these. I saw some of them at the IADA meeting in Munich in 1973. I will mention some of the machines, but not in strict chronological order. Trobas from Graz and Joseph Ries from Zurich constructed the first hand-operated models. Trobas's machine has a simple grid and two tanks. Gross from Vienna used a small cylindrical machine from a paper mill laboratory, but with a large grid added,

Figure 2.121

on which the damaged leaf is placed. The holes are filled one by one by moving the grid under the cylinder. This requires many operations for each leaf. Bergenda, in the Bayerische Staatsbibliothek, designed a hand-operated version, which comprised a plastic tank, wooden rollers with chords for raising and lowering the grid and the perforated plates. Mutville from Paris made a very simple machine of dimensions 57 cm × 41 cm, consisting of two plastic tanks, one inserted into the other. The inside tank has many holes drilled into the bottom. Lorenzen from Flensburg constructed a machine which he called 'Stromer I'. This contains a suction pump, which circulates 70 l of water through two tanks. The machine can be moved on wheels and the working surface is quite large — 46 cm × 68 cm. Vicente Viñas and the Spanish National Centre for the Restoration of Books and Documents have developed a series of leaf casting machines which are now in use in various countries of Latin America, Canada, Europe as well as Spain itself. Recently I received from Mr Laursen of the Royal Library in Copenhagen a description of his machine, which is quite similar to Bergenda's, with chords on rollers.

When I arrived in Israel at the end of 1969, without the drawings of my machine, I set up a laboratory of restoration in the Jewish National and University Library in Jerusalem. I was shocked when I saw how many books and manuscripts in the library were almost completely destroyed. Faced with this situation and with untrained assistants, I had no alternative but to begin building a machine again. I designed a new, improved, model, and we succeeded in building it in 1971. This operated more quickly than the previous models and it was more convenient. We no longer use PVA as adhesive, but sodium CMC (carboxymethylcellulose) instead; and we no longer dry the restored leaves in an electrically heated press. Other small but important improvements were introduced.

This model, called the Recurator, was sold by the Hebrew University to the Library of Congress in Washington, the New England Centre of

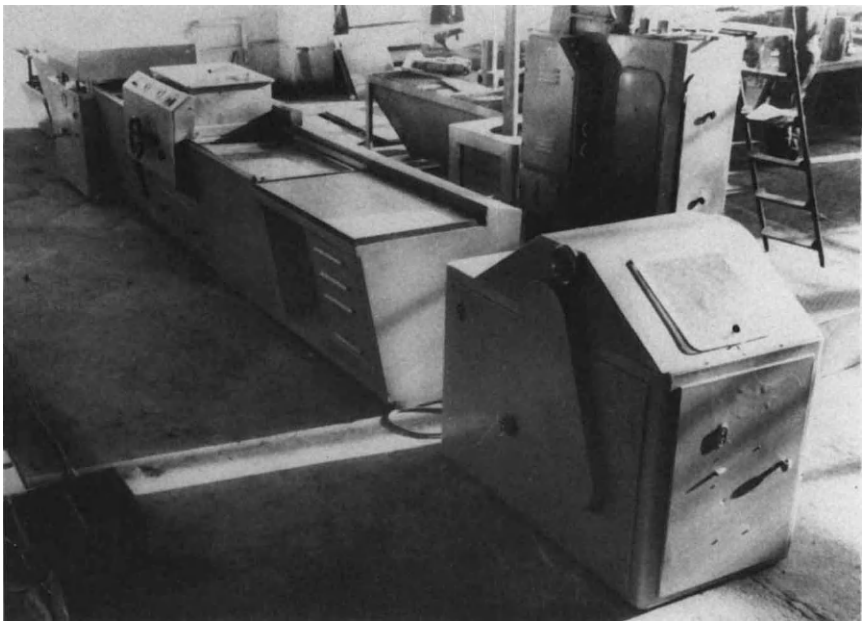


Figure 2.122

Restoration in Boston, the National Archives in Paris and the University Library in Cambridge. The last, initially acquired by Denis Blum and used by him and Guy Petherbridge, is now in the British Library in London.

The last machine, which I want to talk about, is Nyuksha's new model, a description of which was published four years ago. This is a conveyor belt system, consisting of Hollander beater, dosage tank containing the fibre suspension, the leaf casting machine (the upper parts of which are moved hydraulically), a hydraulic press and finally a dryer, consisting of heated rollers. I am sure there are now many variants of leaf-casting machines which are not known to me.

The method of mechanical leaf-casting has aroused much interest all over the world. I recently had enquiries from Singapore, Guadeloupe, Norway and South Africa. It is gratifying that the idea gave an impetus to much novel and clever design. I am sure that the method will be developed to further deal with much severely damaged material.

We owe a great debt of gratitude to the pioneering efforts of Yulia Petrovna Nyuksha and I am glad that I was able to follow her.

2.5.2 Analysis, specification and calculation in the preparation of leaf-casting pulp: a methodology

Guy Petherbridge

Certain current misinterpretations of mechanisms fundamental to successful leaf-casting are discussed and the methodology developed by the author for the analysis, specification and calculation of leaf-casting pulps is described with reference to the leaf-casting system being established at the Canadian Conservation Institute, Ottawa. The necessity for the development and application of an internationally accepted methodology is stressed, based, wherever possible, on standards for paper testing and the monitoring of stock preparation developed in the paper industry.

Introduction

This paper is presented with the intention of dispelling certain misinterpretations of mechanisms which form the very basis of leaf-casting technology whose perpetuation has seriously hindered the development and contributed to the misunderstanding of the real potential of this process. A strict methodological approach based on an understanding of these basic mechanisms is proposed, both in undertaking analysis, specification and calculation in the preparation of leaf-casting pulp, and in the wider framework of the development of leaf-casting units in which establishment of essential equipment, suitable training of specialist personnel, access to sophisticated analytical facilities, liaison with the paper industry research sector as well as the necessary financial support, is systematically coordinated. [1]

Categories of basic equipment

All leaf-casting apparatuses conform to one of two basic categories:

(1) In the category that has seen the greatest development in the number and variety of versions constructed, [2] suitably prepared paper fibres are uniformly dispersed in water in a chamber at the base of which is a paper-making screen on which the damaged artifact is placed. The suspension of pulp in water is then sucked downwards by gravity or various mechanical means and the fibres are deposited on the screen in the missing areas of the artifact. The present paper mainly concerns leaf-casting in this category.

(2) In this category the pulp is introduced by the application of pump pressure from above which forces the paper suspension (at much higher stock concentrations than in the category above) downward into the lacunae. [3] This method has also been used in combination with the first category. [4]

Both these categories exploit the mechanisms of the mechanically induced intermeshing of cellulose fibres in the presence of water and their chemical bonding during the drying process, which are the basis of all paper making from natural vegetable fibres. In contrast to the traditional paper making procedures, however, the paper of the original artifact has already been formed and is merely wetted in the leaf-casting chamber where the new fibres are cast contiguously so that after drying and pressing

they form a satisfactorily stable bond where in contact with fibres of the original. If suitable fibres are selected and suitably treated (*and here is the crux of the matter*) this bonding can occur even in the case of substantially degraded papers and the leaf-cast sheet, although, being a combination of paper produced at two phases, will have the same visual, tactile and overall manipulative and other physical characteristics in all areas whether new or old.

Basic criteria

Given the practicability of the basic concept, three essential criteria must be fulfilled:

(1) Leaf-casting apparatuses must be constructed or available (or modified) which enable the basic paper-forming operation to be carried out efficiently and in a way that all the variables such as evacuation pump pressure can be controlled and monitored.
(2) A detailed standardized methodology of analysis, specification and calculation must be developed and followed.
(3) Precision laboratory equipment producing monitorable and reproducible results must be available to prepare the raw materials so as to give properties which analysis, specification and calculation dictate.

The first criterion is fulfilled and has been for some years. Although in such equipment there is always room for development, both the Recurator,[5] developed after Russian prototypes by Esther Boyd Alkalay, and the Vinyector (Marks 3 and 4), developed after the Eastern European principle by Vicente Vinas,[6] are efficient and reliable in the terms mentioned above. The equipment currently in use in the Soviet Union, principally at the Saltykov-Schedrin State Public Library, Leningrad, may be equally sophisticated— certainly their publications on the subject and their historical role in the development of this field would indicate such.[7] However, the smaller, less complexly engineered machine and hand-held leaf-casters cannot be controlled with the precision which is necessary for producing consistent and predictable results of high quality.

The second and third criteria, surprisingly, have been less conformed to. Although the basic leaf-casting process is a machine paper-making technique related to industrial paper technology, the paper conservation discipline has inadequately utilized the industrial technological and research resources both in expertise and the published literature. Much important and indeed elementary data has been overlooked in this way which would help in a better understanding of both fibre and paper structure and mechanised sheet forming.

Although such already existing knowledge can often be usefully applied to leaf casting stock preparation and the design of casting and drying equipment, there is an area where paper conservators find themselves in frustratingly virgin territory — the physical testing of aged/fragile papers. As Bansa and Hofer have pointed out (see section 2.1.5) current paper-testing equipment and procedures for determining and measuring paper strength characteristics used in paper conservation laboratories are basically those developed for the industrial analysis of recently manufactured papers of a, more or less broadly, homogeneous nature and, because of the destructive nature of most tests, are not generally applicable to the testing and evaluation of historically or artistically valuable aged and fragile artifacts. Even where destructive tests of expendable material for the purpose of experiment are permissible, the testing apparatuses, e.g. MIT Fold Endurance Tester, are designed for substantially more robust papers and cannot cope with the much weaker strength of some antique papers.

As leaf-casting is, above all, a technique uniquely suited to the restoration of extremely degraded papers, the problem is even greater. The reasons are principally: the extreme weakness of the degraded artifact; the difficulty of obtaining a sufficient quantity of uniform samples to conform to the standards of the various equipment types and for statistical analysis because of the often non-uniform pattern of degradation (and corresponding changes in strength properties) across an aged paper leaf and, in the case of leaf-cast artifacts, the complex configuration of lacunae and leaf-cast areas and the bonding zones between them.

Misinterpretations of basic mechanisms and misapplication of technology

Although it is essential that those involved in leaf-casting (and in other areas of paper conservation) pioneer new approaches and methods in the physical testing and examination of aged and weakened papers, ignorance of accessible and firmly established knowledge concerning paper forming and fibre technology has had lamentable consequences in hindering the development of such work and successful leaf-casting itself. Although over the past two decades or so, increasingly efficient equipment has been

developed for the paper-forming stage of the leaf-casting operation (i.e. the leaf-casting machines), the success of whose results obviously depend on the elementary cellulose fibre-bonding mechanisms and the stock preparation treatment, leaf-casting preparatory treatments have paradoxically demonstrated either an ignorance or misunderstanding of these elementary mechanism and stages of manufacture. Misapplication or neglect of the basic principles of paper-fibre chemistry, and stock preparation and beating technology with their attendant effects on both the form of individual fibres and structure of the sheet meant that, although lacunae could be infilled by the available leaf-casting equipment, the bonding achieved was very weak and even rejected in many cases and the achievement of compatibility of the properties of the infill repair paper with that of the original was very much a hit-and-miss affair.

Adhesive casting

Instead of going back to first principles and examining fibre bonding and morphology at a microscopic level, bonding was simplistically considered in terms of 'sticking' and, because of the frequency of unsatisfactory bonding, recourse was had to adhesives with considerable and inventive efforts expended in this direction. Aqueous solutions or emulsions of synthetic adhesives were added to the stuff so that the adhesive impregnated both the original and newly leaf-cast areas of paper. In such practice not only does the machinery have to be designed or modified to cope with the build up of adhesives in the piping systems and require periodic extensive cleaning but, much more undesirable, these adhesives more or less drastically change the tactile and textural character of the original. This is not only an aesthetic response on this author's part but an ethical and practical one. The impregnating chemical is a contaminant of the intrinsic properties and constituents of the original paper even if it does not promote future harmful chemical reactions. Adhesives may reduce the possibility of successful and easy reversal (a primary consideration in the selection of a conservation material). Another aspect, and one which seems not to have been mentioned in the conservation literature, is the way in which exposed paper surfaces covered or impregnated with adhesives may selectively attract atmospheric particulates, and thus over a period of time are either more or less soiled than adjacent untreated sheets of originally similar compostion.

Adhesives are also used as a short cut to overcome discrepancies in bulk between the new and old paper. Excess bulk is held down by the adhesive during pressing and drying. The addition of adhesives, while in some cases assisting dispersion of the fibres in water, increases the viscosity of the stuff, e.g. in the case of Primal AC73, which creates, at the last moment of evacuation of water from the leaf-casting chamber, a viscous 'lip' of stuff along the edge of the lacunae. The vacuum action of the leaf-casting apparatus, as it is now drawing air as well as liquid through the area of least resistance — the newly leaf-cast infills — cannot withdraw this viscous lip which retains paper fibres. On drying these form an obscuring deposit and also make this zone slightly thicker and less flexible than its neighbours. Damage may occur along this zone because of the contrasting flexibilities. Leaf-cast areas impregnated with such adhesives also tend to be more rigid (denser and less porous) than the paper of the original artifacts, particularly in the case of hand-made printings.

Inadequate stock preparation

An almost endemic weakness in leaf-casting procedure is the inadequate preparation of the paper pulp itself. Although an acquaintance with the basic techniques and stages in the traditional and modern processes of manufacture of paper—the isolation of individual fibres from their original plant or textile source followed by various essential refining and beating processes—as well as a knowledge of the fundamentals of paper structure, would seem *de rigueur* in a paper conservator's education, this knowledge, illogically, has not been applied to problems in leaf-casting technology or, if so, in a rather primitive way. The elimination of any proper beating regime is characteristic with, instead, recommendations for the use of a domestic or industrial blender as a substitute stock-preparation treatment. Thus we find the blending of old papers 'of the same type and tone' as the original and of paper pulp in dried sheet form without any real consideration of the characteristics of these materials prepared in this way[8]. Even the possession and use of a laboratory beater is not sufficient if there is too limited a range of pulps and beating regimes whose choice is not based on a considered analysis of the complex individual requirements of the very diverse kinds of paper and fibre-bonding problems encountered in actual practice.

This phenomenon of neglect of basic paper-making principles and equipment is admittedly in most cases based on economic restrictions limiting specialist training and acquisition of what is, in terms of the frequent low level of expenditure in paper-conservation facilities, expensive apparatus, but it has nevertheless resulted in patterns of unsuccessful casting which have caused a number of

conservators to discontinue involvement with the process and potential funding sources to deny support. The author's approach has been to return to first principles and, accepting that suitable casting equipment is available, to investigate and develop the practice of leaf-casting without the use of added adhesives (except in those circumstances where an admixture of synthetic fibres would be beneficial as outlined above).

Before repulping aged or recent papers for leaf-casting or manual infill repairs, certain factors should be taken into consideration. Paper fibres after manufacture are subject to a phenomenon of irreversible hornification which contributes to altered morphological and structural characteristics in paper formed from repulped fibres. Aged papers are additionally degraded in varying degrees and contain degradation products which, although removed to some extent in the water associated with beating and casting, may still present a potential danger to the leaf-cast sheet. Because of the fragile state of the aged constituent fibres these suffer damage when rebeaten or possibly even when disintegrated (i.e. in a laboratory disintegrator). Except in the case of waterleaf papers, reused papers contain various sizing materials whose close association with the paper fibres can cause problems in the achievement of an even dispersion of fibres in the stock and inhibit fibre bonding. This factor of the 'encapsulation' of fibres by the sizing material can also cause a problem when present in the original artifact and hinder the bonding of the newly cast fibres to those of the original. In practice this seems to be less of a problem with gelatine-sized papers than those with rosin or more recent synthetic sizes. This is possibly because the gelatine more readily decomposes through fungal attack and both in its undegraded (at higher temperatures) and degraded state is more readily soluble in water than the other sizes.

With regard to the practice of using domestic laboratory blenders: these are not designed for the beating of paper pulps but may do so to some extent — James d'A Clark (1978) and others have done some work in assessing the strength increase of papers produced from pulp stirred in a British or TAPPI standard disintegrator which may have implications for effects produced in a blender. Brian March of the CCI leaf-casting laboratory is also carrying out quantitative and qualitative testing in this respect. However, blenders should not be considered as cheap substitutes for laboratory beaters and can cause undesirable modifications, particularly if large concentrations of long cotton and bast fibres are blended for too long. For the disintegration (as opposed to the beating) of pulps the specially designed apparatus — the laboratory pulp disintegrator (see below) — should be used. It produces regulated and even dispersion of pulp.

Paper pulp as supplied in sheet form may not be beaten/pre-refined and often merely represents an interim stage in stock preparation (except in the case of groundwood) the paper fibres have reached after being separated from their original virgin state in association with other unwanted vegetal structures and chemicals. Although temptingly convenient to use in this form without further modification, versatility of application is limited without further beating. Before beating such pulps they should be left to soak for a time (paper fibres swell substantially in water so that the available surface area for bonding increases greatly). Unbeaten sheet pulp forms a furnish of relatively high freeness which produces a bulky paper of little strength. The individual fibres, particularly textile and chemical wood, have their outer cell wall relatively intact and are thus correspondingly impervious to water. These factors and the fact that the fibres are still of some length can, however, be exploited in pulp blending for attainment of leaf-cast papers of certain calculated characteristics.

Synthetic fibre casting

Although, whenever possible, we should try to develop maximum reliance on unaided fibre-to-fibre bonding, in the case of badly charred, chemically corroded or extremely mould-debilitated material there is a justification for the use for another form of synthetic adhesive—polyvinyl alcohol in fibre form (added as a small proportion of the leaf-casting furnish) which behaves like a cellulose fibre in dispersion in water and in paper forming but which can later be heat set. This approach has been developed in the Soviet Union and some details published[9], although not in sufficient detail to replicate. Our leaf-casting unit at the Canadian Conservation Institute with the assistance of the Pulp and Paper Research Institute of Canada is embarking on investigations in this field.

Following reports from the Soviet investigators, it was decided to enter into further experiments along these lines. Attempts to obtain further details from Leningrad beyond the sketchy details in the literature, having met with no response, we ultimately were most fortunate in obtaining the assistance of PAPRICAN who supplied some samples of PVOH fibres of Japanese manufature which seemed to fulfil the necessary criteria.

Preliminary investigations indicate that, of the PVOH samples obtained, Kuralon VP 101-4 has a definite potential application in leaf-casting.

Although the publications on these fibres by the manufacturer, Kuraray Co. Ltd.[10], do not give specific details of this particular fibre it is assumed that it is closely related to Kuralon VPB 101. This is characterized as a 'non-heat-treated and non-formalized fibre, 1.5 dr, readily soluble in water at 70°C, moisture content: wet 60%, dry 5%'. It should be dried (i.e. heat-set) at 60-70°C. Comprehensive details of these fibres are listed in the Kuraray technical data publications so they will not be set out here.

Castings of this material were made without any admixture of any other fibre and formed very even (though transparent) sheets and other sheets were cast of a mixture of 10% VPB 101-4 and 90% semi-bleached Kraft (PFI 2500 rpm, standard gap). Test casts were also made of this mixture in missing areas created for experimental purposes in modern machine-made, chemical wood furnish paper which produced extremely tenacious bonding. All these castings were dried in a laminating press in the recommended temperature range between 0.6 mm sheets of Teflon. Further experiments with these fibres must be carried out. These should include researches into suitable solvents with which to reverse the adhesive bond between the original and newly cast areas.

Specifications for casting of recent and degraded papers

To achieve casting in any given paper leaf of a new paper which will not only successfully bond (without the assistance/interference of adhesives) to the original but will have the same or a sympathetic tone, the same caliper, bulk, surface characteristics, manipulative and strength properties without overlapping or obscuring the original surface, requires a discipline based on precise analysis and calculation. The task is additionally complicated because, although it is possible (following the methodology outlined below) to replicate the original furnish and approximate the stock preparation and finishing for modern writings and printings, particularly handmades, the type of material most suited for leaf-cast repair and which, as conservators, we are most likely to treat, are aged, degraded papers. In these cases it would be ethically irresponsible and certainly technically ridiculous to produce leaf-cast repairs which reproduced the deteriorated materials of the original.

From an analysis of the original's constituent materials and manufacturing treatments and its physical properties, a specification must be designed for a leaf-casting furnish which, while of permanent and durable fibres (and other additives) of a different form or type from those of the original in its aged state, will yet look and behave in all ways compatibly when suitably cast and finished.

Non-discriminating use and preparation of materials and calculations based on mere visual assessment will not produce consistently reliable results. Leaf-casting does not allow much margin of error. The major desiderata are interrelated—either the repair bonds and has sympathetic textural and mechanical characteristics or the failure to achieve one result will affect the achievement of the others.

In order to establish a viable leaf-casting system a methodology of analysis, specification and calculation must be formulated and a substantial financial commitment made to acquire the essential equipment, to fund operators and advisory personnel and external analytical work. There are few short cuts in establishing the initial system though substantial savings in both money and effort could be made if the currently widely dispersed leaf-casting units would agree to a research and production methodology so that basic data could be assembled in co-ordination and freely interchanged. Between 1978 and 1981 the author established a leaf-casting system (*see Figures 2.123* and *2.124*) for the Works on Paper Division of the Canadian Conservation Institute, Ottawa. The following part of this paper describes the methodology of analysis, specification and calculation developed by the author and the equipment designed to execute it in this unit. Limitations on space do not permit exhaustive treatment of each operation. Rather this paper is presented as an acknowledgement of the enormous potential for further research and development in this field.

Analysis of original paper

In order to produce specifications for furnishes and finishing treatments which will result in leaf-cast papers compatible with those of original artifacts, we must first of all investigate the materials and properties of these originals. Given the restrictions referred to above regarding the use of conventional testing equipment for evaluating physical strength properties of aged and weakened papers, it may be useful here to briefly discuss those properties by which papers are commonly characterized and those tests which may or may not be applied in the context of original artifacts. In the printing, paper and packaging industries testing apparatus and procedures for the assessment of many properties, mainly relevant to the end use or elaboration of their products, have been devised and standardized.

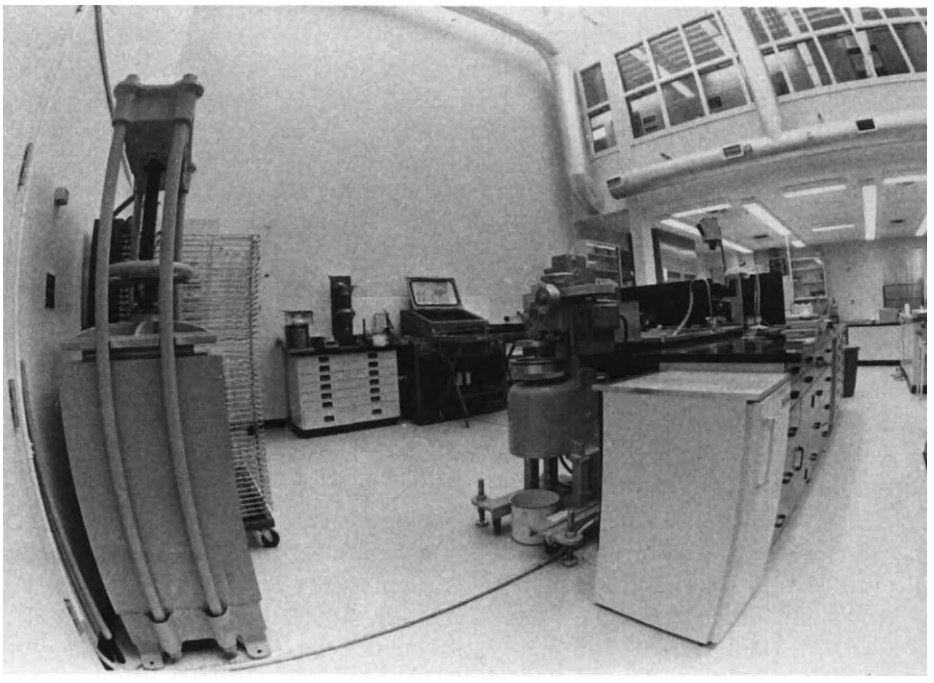
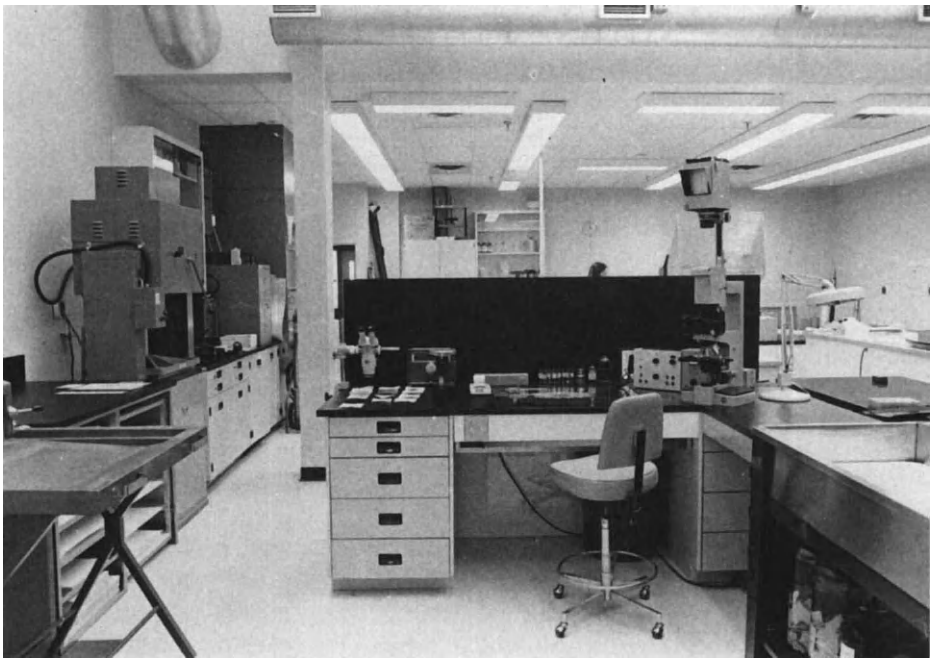


Figure 2.123. Leaf-casting unit, Canadian Conservation Institute, Ottowa. Pulp preparation, casting and drying areas.

Figure 2.124. Leaf-casting unit, Canadian Conservation Institute. Analytical/calculation and pressing areas.



Although the following list is not exhaustive, these are amongst the most commonly recorded properties[11].

(1) Substance;
(2) Thickness (caliper);
(3) Bulk;
(4) Bursting strength;
(5) Burst/weight ratio and burst factor;
(6) Breaking length;
(7) Tensile strength;
(8) Dynamic tensile strength;
(9) Folding endurance;
(10) Wet strength;
(11) Tearing strength;
(12) Rigidity/stiffness;
(13) Gloss/finish;
(14) Smoothness;
(15) Opacity;
(16) Sizing;
(17) Surface/penetration;
(18) Porosity;
(19) Absorbency;
(20) Oil absorbency;
(21) Moisture expansivity;
(22) Hardness;
(23) Surface stability.

Of these properties only (1), (2), (13), (14) and (15) are evaluated by apparatus or techniques which are non-destructive to the original sheet of paper. Of course, we can use these methods to determine the strength and manipulative properties of sample sheets produced by leaf-casting but the results cannot be profitably compared with the original papers which we may not damage or destroy to obtain testing data.

Notwithstanding, as will be explained in more detail below, we should utilise wherever possible those standardized non-destructive methods which are in practice, to assist us to control, monitor and record leaf-casting operations at whatever stage and intercommunicate, using the common language provided by these standards, information gained with our colleagues in conservation, science and industry.

In leaf-casting analysis the following characteristics and properties of original papers must be determined and a standardized system formulated by documenting them for comparative purposes:

(1) Fibre type;
(2) Sizing material;
(3) Non-fiberous fillers;
(4) Moisture expansivity (dimensional instability)
(5) Colour;
(6) Surface smoothness/finish;
(7) Thickness/caliper
(8) Bulk
(9) Substance
(10) Rigidity.

To determine the constituent fibres, microscope slides are prepared for examination by transmitted light. We use Chlorazol Black E stain which is permanent, offers good contrast, both for photography and enhancement of morphological features.[10] A photographic record should be assembled of both characteristic and unusual fibres and fibre states (photographs should be taken at standard magnifications for comparative purposes). Our laboratory is equipped with a Leitz Orthoplan biological microscope with built-in 35-mm and large-format cameras and colour-correction system. Our fibre-identification file includes slides (and photographs) of sample fibres that can be expected in the Canadian context. These are built up principally from the examples obtainable from the TAPPI Fibrary of the Institute of Paper Chemistry, Appleton, Wisconsin, as well as from the standard pulps we use for leaf-casting. Standard chemical spot tests (aniline sulphate and phloroglucinol/-hydrochloric acid) are used for verifying the presence of mechanical wood furnishes. It is important to have in the leaf-casting unit a good range of fibre atlases and other pulp-identification literature.[13]

Spot tests are relatively straightforward for determining the presence of rosin, gelatine and starch sizes and a number of destructive tests are available for the identification of gelatine, casein and modern plastic resins but the latter are really a matter for the advice of a specialist in this subject.[14]

The identification of non-fibrous fillers and coatings is important in a wide range of papers from the eighteenth century onwards where they have been intentionally added to improve opacity, printing quality and brightness. Conventional destructive tests based on the amount and character of ash obtained from combustion of the paper according to various standard methods can not be used in the conservation context. Therefore one must resort to chemical microscopy using traditional instruments or, better still, a scanning electron microscope in conjunction with X-ray diffraction analysis. Browning outlines the range of available techniques and a bibliography.[15] As yet, to the author's knowledge, no systematic investigation into the application of fillers to leaf-casting has been undertaken, but if the leaf-casting process is to be of real contribution to the conservation of material on machine-made papers this work must be advanced.

It is important to be able to make an assessment of the moisture expansivity (and, conversely, contraction) or dimensional instability of papers to be leaf-cast as it is vital that this property should correspond with that of the leaf-casting repair paper. Otherwise the tensions set up during drying after casting between the newly cast and the original paper, as well as in reaction to later changes in environmental relative humidity, may cause more or less severe cockling, with the attendent risk of these tensions overcoming the strength of the fibre bonds at the contact zone and consequent rupture. Even a degree of cockling which may seem minimal in a single leaf can, if multiplied, cause great distortion in a bound book block. The cumulative stress is considerable and can eventually lead to the structural breakdown of the entire volume.

Although conventional laboratory devices for the testing of moisture expansivity such as the Fenschel Wet Expansion Tester (made by Schopper) are destructive and thus out of our context, the author uses a modification of a simple principle utilized by the PATRA Paper Equilibrium Tester and CPPA Standard C4. A small stainless steel metal gauge is made which makes two very fine needle puncture marks 5 cm apart on either the wetted-out original sheet or the freshly cast sheet after its first pressings. These are then allowed to dry in blotters in a standing press following our standard procedures *(see page 172)* and then the shrinkage, expressed as a percentage, is measured and recorded. This provides us with data on the comparative shrinkage rates of newly leaf-cast and adjacent original areas. Similar tests on wetted-out original papers and on our sample control sheets *(see page 173)* are carried out with the papers dried without restraint to provide quantitative data on their expansion and contraction in storage and in use (testing in our laboratory is carried out in controlled room temperature of 20°C and relative humidity of 55% RH). The very small impressions produced by this testing method do not cause permanent damage to the paper and can be closed with a hand tool after testing.

Although the eyes of no two human beings respond exactly the same in the determination of colour and shade and although relatively sensitive equipment such as colour difference meters do exist and has been useful in conservation analysis,[14] the human eye can still cope much better with variables such as texture and changes in colour according to the light source by which a paper is viewed. The author thus prefers to build up a large 'palette' or album of samples whose furnish, etc. is recorded and codified. The natural tones of these samples produced from standard pulps and treatments and by the admixture of permanent non-injurious colouring agents can be compared with that of original paper artifacts and thus, together with the consideration of other variables in the selection of compatible furnishes, a casting sympathetic with the original can be obtained.

Although testing equipment and non-destructive methods do exist for determining surface smoothness and finish, these have been developed with the concerns of the modern printing industry in mind and are not particularly relevant to our needs, especially in the case of earlier handmade papers. In any case, as for the evaluation of colour and shade, no artificial aid can match the human eye in the perception of similarities or differences in surface finish and texture. The only problem is in the quantitative documentation of such observations for future comparative purposes. As in the selection of matching or sympathetic colours one must build up an album of standard papers produced from a range of standard pulps and pulp combinations, beaten, dried and finished in various ways from which, in combination with other factors, one can produce a suitable specification for a repair pulp.

Machine-calendered, hot-pressed and hand-burnished finishes are particularly susceptible when wetted at various stages of the leaf-casting process (principally during initial conservation treatments such as washing, re-sizing and the leaf-casting process itself). The surface fibres swell and on drying reorientate themselves so that the original polished surface is lost. One can, by hand burnishing with various tools and drying in contact with various smooth surfaced materials, reproduce the original surface, but such 'restoration' is not desirable and one should seriously consider other conservation techniques for these categories of material.

Obviously the thickness of the leaf-cast areas must be the same as that of the original paper, otherwise discrepancies would cause preferential flexing zones to develop along which damage would eventually occur as well as creating problems in the binding and dimensional stability of assemblages of leaves with uneven thickness profiles. Our unit is equipped with a Cady 12" DW Micrometer[17] with interchangeable metric dials graduated in microns and a dial graduated in 0.0005 in. The 12in 'Deep Throat' allows measurement of thickness at any point on a 24 in square sheet of paper. Thus any sheet which can be accomodated on either the Vinyector or Recurator casting screen can be measured. (For further details of our system of caliper measurement *(see pages 173 and 174)*).

Bulk is a measurement of paper density and it is important for the stability of the entirety of a leaf-

cast artifact that the new and old areas of the leaf cast are of equal bulk. This is a measurement of the ratio of the air space to solids within the sheet and is conditioned by the type of fibre employed, its refining, beating and drying treatments and the surface finish applied:

$$\text{Bulk} = \frac{\text{Thickness (in microns)}}{\text{Substance in grams per square metre}}$$

In a leaf-casting unit this property can be measured using conventional methods and equipment. [18]

Substance expressed as grams per square metre (gm^2) is easily calculated, using conventional laboratory apparatus for the determination of area and weight. Because in leaf-casting one is often required to repair damage to a single light weight leaf, a very sensitive balance, which can yet be practically used in a workshop context must be acquired. In our unit we use a digital balance with a fairly large pan [19] which allows rapid determination of the weight of paper leaves to 0.001 g.

Assessment of rigidity or stiffness is a major factor in the selection of a suitable repair paper for any individual paper artifact by whatever conservation process, and is particularly crucial for successful leaf-casting. Unfortunately, once again, testing methods developed for the paper and printing industries are not appropriate as standard sample sizes must be cut out of the paper being tested and are designed primarily for the evaluation of machine-made papers. One therefore must make a subjective judgement of this property based on comparison of the original artifact with sample sheets of the same substance, bulk, etc. prepared from a standard range of leaf-casting pulps. It should be noted here that present leaf-casting equipment cannot replicate the 'grain' direction of fibres characteristic of most machine-mades with associated difference in flexibility with and against the grain.)

While the individual characteristics and properties listed above might well be measured in the course of conventional paper conservation, the whole range must be assessed in leaf-casting analysis and their interrelationships observed in order to be able to design and specify compatible papers. We must also examine the original artifact in particular detail to determine the type of treatment used in the original pulp preparation as well as the present state of the paper's microstructure to determine its bonding potential. Such examination will determine the following factors affecting successful bonding of new fibres to old and influence the selection of a suitable furnish: state of degradation of the original fibres and of fibre bonding (this may influence the elasticity of the paper — it is important that this characteristic be matched by the leaf-cast areas); potential bonding area and length of fibre along damaged edges; amount of detritus formed by decomposition products and those acquired such as atmospheric particulates, dirt and oils from handling which encrust or coat fibres surfaces and fill fibre interstices. Visual examination and handling will give some initial indication of the original beating treatment if degradation has not progressed too far.

Characteristics induced by beating

Even if a single type of fibre is used, different properties can be produced in the final paper sheet by varying the beating treatment. For example, different stock concentrations, use of blunt or sharp beater bars and altering the gap between the bars and the bedplate so that the range of actions from cutting to rubbing, can produce a stock ranging from 'free' or fast-draining to 'wet' or slow-draining. These beating regimes have characteristic effects not only on the formation and properties of the sheet as a whole but on indivdual fibres. Examination of prepared microscope slides or of paper specimens by scanning electron microscopy can, with experience, give some indication of these stages of original manufacture. Thus a cotton blotting from a furnish beaten in a light stock concentration and using a sharp tackle will have a significant proportion of distinctly cut fibres, whereas a rag loan of a cotton and linen furnish beaten at a higher stock concentration and using a blunt tackle, which rubs rather than cuts, and for a longer period, will have extremely split and fibrillated cotton fibres with the linen remaining much more intact, though with characteristic 'frayed out' fibre ends. [20]

Beating can vary from light or 'free' (just sufficient to disperse and separate fibre clumps where bulk, opacity (and porosity in the case of longer fibre types) are the desired features) through medium (where a combination of cutting and wet beating produce more fibrillation and strength) to 'wet' (where the treatment is much heavier and extended and the resulting fibres very bruised, split and fibrillated). Thus we can range from unbeaten, intact fibres where the outer cell walls are relatively insoluble and resist permeation (thin, thick-walled fibres such as flax are less porous than thin-walled ones such as cotton and mechanical wood); the fibres are relatively rigid and thus do not intertwine as much as beaten fibres; the surface area available for contact and bonding is minimal; and cellulose debris and hemicellulose are not available to perform an additional cementing function — all

contributing to a basically porous, bulky, opaque and relatively weak paper — to the other extreme where, with extended and heavy beating and consequent fibrillation and other fibre modification, the surface area of fibres (potential bonding area) and the degree of intertwining increases, as does a certain adhesive function of the cellulosic matter rubbed off the fibres (a large amount of fibre debris is lodged in the fibre interstices) and of hemicellulose, resulting in a dense, tenaciously bonded and transparent sheet. The latter papers tend to be relatively inflexible with a pronounced rattle and are more impervious to liquids than papers from free beaten stock. A wet beating regime produces a pulp where the fibres are swollen and contains a high proportion of water and is slow-draining. Papers produced from them are subject to a high degree of shrinkage on drying, a negative factor in the production of leaf-casting pulps. At its most extreme, beating will produce a state where increasing damage to the fibres, particularly in the reduction of fibre length, will counteract the bonding and cementing effects so producing a brittle paper, weak in strength, tear and folding resistance.

It must be kept in mind, however, that features such as transparency can be a result of other treatments, e.g. coniferous chemical wood pulps tend to be more transparent, and the examination of fibre and paper structural characteristics to determine beating treatments must be carried out in conjunction with the identification of fibre species (type) and a knowledge of the effects of the preparatory stages of chemical and physical processing to separate the pure fibres from their original vegetable source. For example, because of the resulting fibre

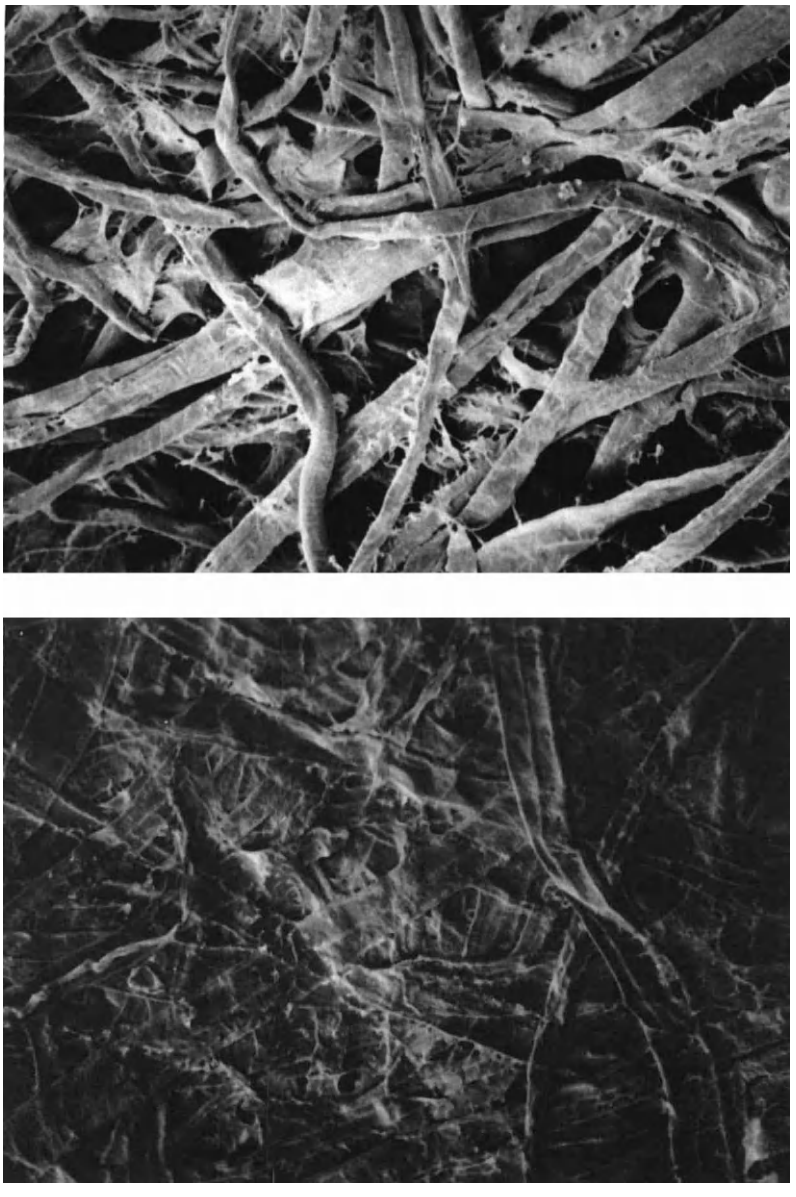


Figure 2.125. Scanning electron micrographs (×200) demonstrating relative effects of (top) very free beating (bleached cotton liners) to (bottom) wet beating (western red cedar unbleached Kraft) in leaf-cast papers.

lengths, even unbeaten fibres of different types will produce papers of different characteristics. Cotton linters and textile linen, with high proportions of pure cellulose, require light chemical treatment to remove unwanted constituents such as lignin, so that the original fibre length is relatively unchanged and, unbeaten, produce a relatively strong, bulky paper with an uneven surface *(Figure 2.125)*. On the other hand, the physical and chemical treatments required to remove high proportions of undesirable constituents in grass and cereal fibres result in reduced fibre length and a paper bulky and with a close, even surface but with little strength compared with an unbeaten cotton or linen paper.

As discussed below, it must also be remembered that the blending of furnishes of different fibres and/or treatments (as well as loadings), exploiting the special characteristics of each, has been a regular phenomenon in the history of paper making reaching particular complexity in machine-made papers, and this must be considered in analysing the original manufacture of a paper sheet.

Certain broad categories of initial treatment processes (and also species) can be identified by the treatment-specific colours produced by staining fibre samples for microscope examination with agents such as Herzberg's Reagent, the Alexander Stain, the Selleger Stain, the Wilson Stain, C Stain, etc.[21] Selective use of these stains enables differentiation not only between a wide range of fibre types but also the initial separation treatments (groundwood, sulphate, sulphite as degree of cooking, etc.) as well as between bleached or unbleached fibres.

Binocular microscope examination, with raking and overhead light, of the surface of the original sheet should also be carried out to try to determine the original finishing method by qualities of surface texture as well as type or print impression and marks left by the pressing felts. Such characteristics we must be careful to preserve and will influence the selection of a compatible support material on which to cast and suitable leaf-casting drying and finishing methods.

All these interrelated features of the original artifact can be of significance in leaf-casting both diagnostically, in determining the original manufacturing treatments, and in the specification and preparation of repair furnishes and subsequent processes.

Scanning electron microscopy

Examination of the individual constituents of a paper sheet using transmitted light microscopy, stains, chemical spot tests and the properties of these constituents as combined in the sheet and of surface formation and damaged edges gives us a certain amount of useful data. However, for the purposes of designing or selecting a compatible leaf-casting furnish we really need detailed information about the condition and physical structure of the paper web as a whole, internally and externally, and of its individual components *in situ* rather than as reflected in its mechanical properties or in its reactions to various testing stresses and chemicals.

For this inspection of a paper in its 'undisturbed' state scanning electron microscopy can be most usefully employed. Techniques as well as published data relating to the use of such equipment in the paper industry have increased over the last two decades[22] but, principally because of the high capital costs (though, with the recent explosion of technology using microprocessors, equipment is becoming less expensive and more versatile), its potential is only just beginning to be realised in the paper conservation field.

In the scanning electron microscope, imaging of surfaces is normally accomplished by utilization of emitted secondary electrons arising from impingement of the primary beam. The collected signal is used to synchronously modulate the brightness of various cathode ray tubes or a fast-scan television tube so that each point of the specimen is represented by a corresponding point on the observation screen. Using this equipment, one can examine in very great detail and with a great depth of field the actual physical form and condition of a paper at magnifications ranging between $\times 5$ and over $\times 30000$, although for our purposes the range $\times 100$ — $\times 3000$ is generally sufficient. The Analytical Research Services Division of CCI has such equipment as well as apparatus for X-ray diffraction analysis, which enable one to either scan any selected image area to determine the constituents of such additives as non-fibrous fillers and their relative location and proportions, or to be able to analyse in detail any one point in the imaged area, e.g. to identify a cystalline occlusion.

For the purpose of leaf-casting examination one can profitably work from specimens as small as 3 mm square, although slightly larger specimens are prepared from our leaf-casting paper samples prepared from our standard pulps. Specimens are first adhered to a metallic specimen stub with a carbon paint and then coated by evaporation with gold at low pressure to avoid build up of charged fields and to increase secondary electron emission.

As the leaf-casting process has evolved, various generalized accounts of the mechanisms operating in the bonding of newly cast fibres to original paper fibres have been forthcoming, based on superficial

examination and on analogy with the mechanisms of fibre bonding and sheet formation as described in the literature and investigations of paper chemists and technologists. However, to the author's knowledge, and certainly not in the literature, no systematic programme had been initiated to date to utilize SEM for leaf-casting research — an approach which, given the restrictions outlined above on the application of most conventional paper testing procedures to aged and weakened artifacts, would seem to offer much potential.

At CCI, therefore we have initiated an investigation into the morphological and structural characteristics of fibres and sheet formation and of bonding and other mechanisms of adhesion between the fibres of degraded and leaf-cast artifacts, concentrating in particular in the zones of contact between the old and new fibres along torn and cut edges. We are also interested in ascertaining the degree of penetration (and of possible strengthening) and deposition of leaf-cast fibres at the artifact surface (obscuring text or other image). It is hoped to eventually be able to relate characteristic observed structures and sheet condition to specific physical properties, manipulative characteristics, etc.; also by reference to new samples produced under controlled conditions, to ascertain the beating regime of the original, and to assess the bonding potential of the artifact fibres in order to be able to develop precise specifications for repair furnishes and drying and furnishing treatments. Specimen sheets prepared from leaf-casting pulps whose fibre furnish, beating conditions and drying and pressing (finishing) treatments are known (and artificial ageing conditions) are being investigated to provide standard comparative data for the evaluation of original material.

In spite of the lack hitherto of specifications based on actual rather than theoretical or deduced knowledge of the leaf-casting bonding mechanisms, non-adhesive techniques resulting in stable bonding, based on both theoretical principles and empirical data, have been developed. There are, however, some recurrent circumstances when bonding is characteristically rejected and for which no entirely satisfactory explanation or practical solution has been forthcoming. Our research programme therefore incorporates an examination of castings presenting these problems so that we can make detailed visual comparisons at a microscopic level of successful and poor or rejected bonding. Already the evidence obtained is contributing to a solution of these problems (*see Figure 2.132*). Similarly, it is hoped that experimental results in the use of synthetic fibres in the leaf-casting of chemically corroded and burnt papers also may be assessed.

Although by examination with the naked eye and by conventional optical magnification systems there appear to be no significant changes in the surface profile of leaf-cast artifacts if suitable casting screen material and drying methods are used, scanning electron micrographs of representative paper surfaces before and after successive treatment and casting stages can supply corroborative evidence (or otherwise). The assembling of such documentation is of particular value in the assessment of the relative effects and practical application of casting support materials and drying and finishing processes. (This section of the paper is presented not as a series of definitive conclusions but as a brief progress report indicating the value of this avenue of investigation and in the hope that other leaf-casting units may be stimulated to carry out similar work and co-operate in the exchange of information so that we may build up a common data bank documenting the structural and morphological characteristics of leaf-casting produced under controlled conditions as well as of problem phenomena.)

The preliminary stages of this investigation have concentrated on a group of papers produced from our controlled standard furnishes and blends and cast to a group of handmade linen papers from dismembered eighteenth century and early nineteenth century Romanian and Greek printings. Characteristics of sheet formation and fibre morphology and other surface features are being examined (1) before any conservation treatment; (2) after washing (and drying); (3) after resizing (and drying) treatments; (4) after leaf-casting and drying following our standard procedure for our testing specimens.

The SEM investigations to date would seem to indicate that provided that the fibre complex of the edge or other surfaces that are intended to be cast to offers sufficient potential bonding area: provided that the mechanics of the leaf-casting system enable maximum contact and intermeshing of the new and old fibres to take place along the casting zone; and provided that suitable new fibres are prepared and beaten so that they are able to conform to the micro-contours of the edges of the original artifact so that intermeshing is maximized and the maximum surface area of the new and the old are in contact, then bonding, on subsequent drying and pressing, must take place. It then should not be disrupted unless unequal rates of shrinkage on drying and later responses to changes in relative humidity create tensions which the bonds cannot withstand.

Although new fibres are being married to old, the normal chemical (hydrogen) bonding mechanism and physical interweaving on which the formation

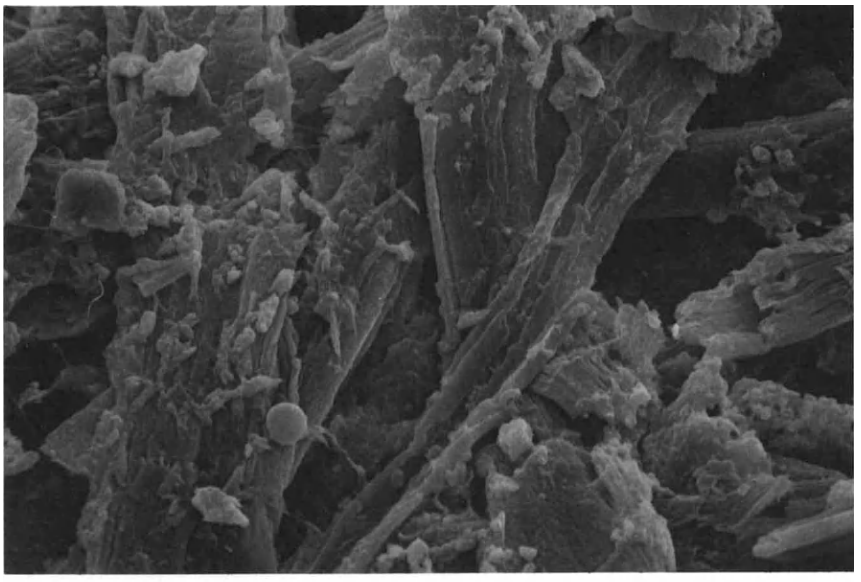


Figure 2.126. Scanning electron micrograph (×1000) of fibres of a mid-18th century Romanian printing showing advanced state of degradation.

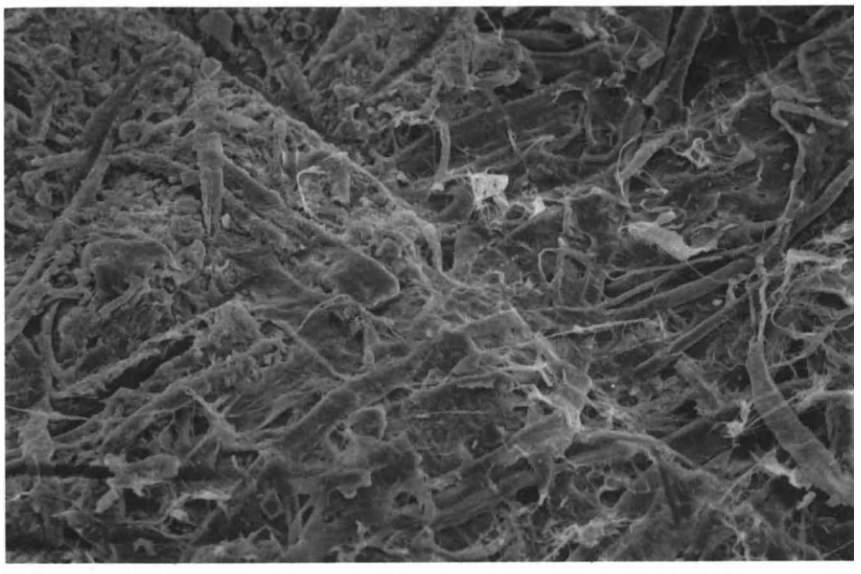


Figure 2.127. Scanning electron micrograph (×200) of the same leaf as Figure 2.126 showing the original paper on the left and the leaf-cast area on the right. Though both the fibres and the sizing medium of the original are so degraded, satisfactory intermeshing is occurring along the contact zone with bonding and adhesion clearly visible at higher magnifications as in Figure 2.128.

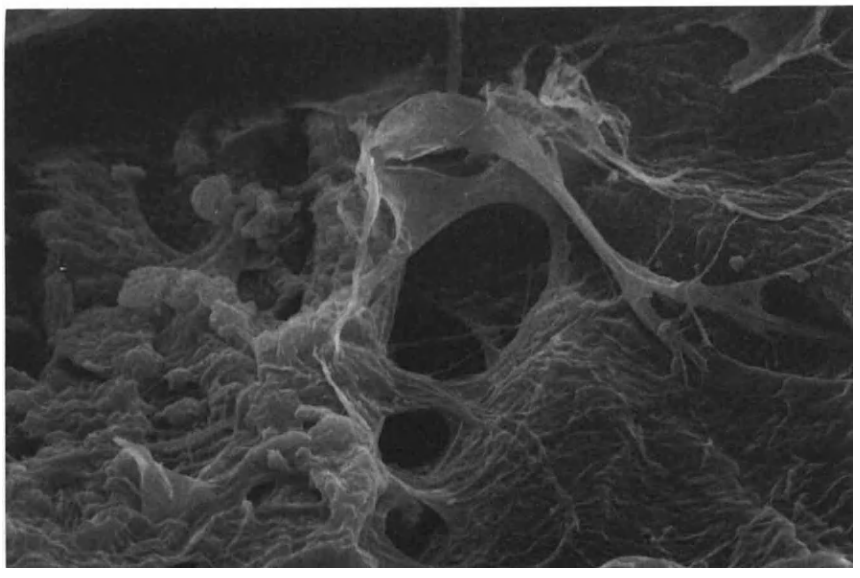
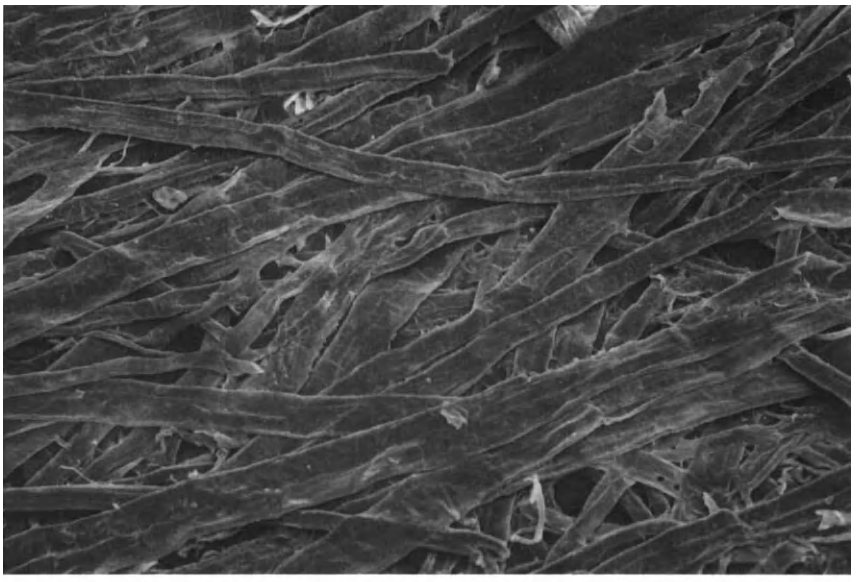
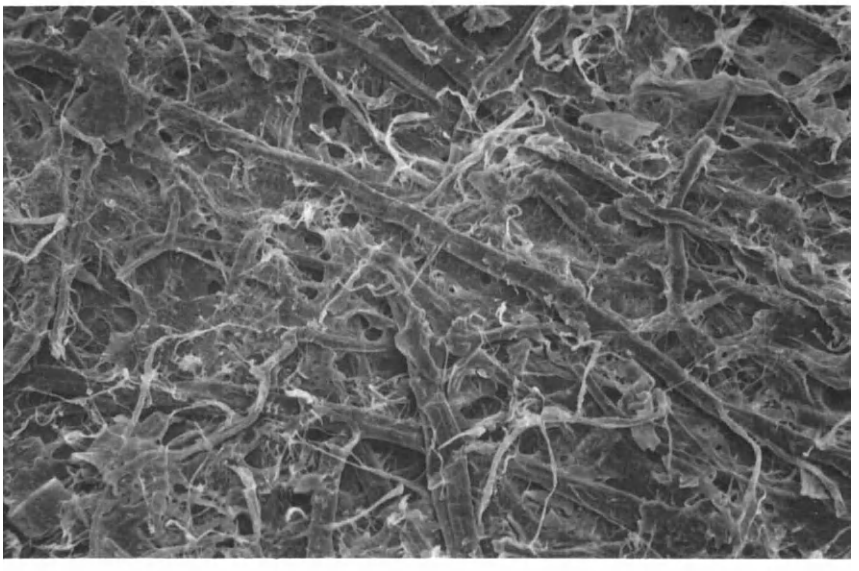


Figure 2.128. Scanning electron micrograph (×2500), showing contact zone between leaf-cast fibres (semi-bleached Kokanee Kraft) on the right and original fibre (linen) on the left.





Figures 2.129 and 2.130. Although light weight, the original paper (Figures 2.126-128) was of relatively high bulk and had been medium beaten and little sized with an uneven surface. Bonding between its fibres and adhesion of associated materials had greatly weakened through degradation, making the paper very inelastic with its paper fibres swelling minimally when wetted and its structure tending to break up rather than return cohesively back to the state of normal moisture content. Its bulk, however, was retained and it was still relatively porous: (i) an unbeaten semi-bleached Kokanee Kraft (Figure 2.129 shows a leaf-cast paper from this pulp × 150) and (ii) a medium beaten unbleached flax (pre-cut to 4mm) (Figure 2.130 shows a leaf-cast paper from this fibre × 150). The semi-bleached Kraft was selected because the rigidity and scale of its fibres and the relative impermeability of its cell walls coupled with the high ratio of air to fibre in the leaf-cast sheet (this fibre received in pulp board form and not soaked before disintegrating to preserve the relative unsuppleness of the fibres and so that any swelling and subsequent shrinkage on drying would be minimized) would equate to the bulky, porous but ineleastic degraded original with the flax with its characteristic fibrillated fibre surfaces providing bonding, and assuring intermeshing at the contact zone between old and new fibres and giving compatible flexibility to the new areas. The combination of both pulps provide a surface and colour very close to the original.

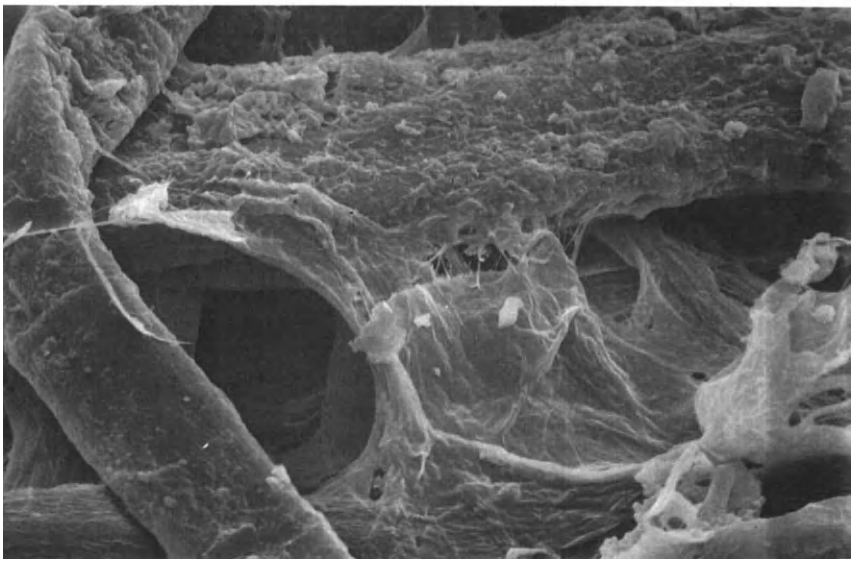


Figure 2.131. The contact zone of the above-mentioned example showing the characteristic flax fibrilation so useful in leaf-casting of early handmades (new fibres at the lower level, old fibres at the upper). (×1000).

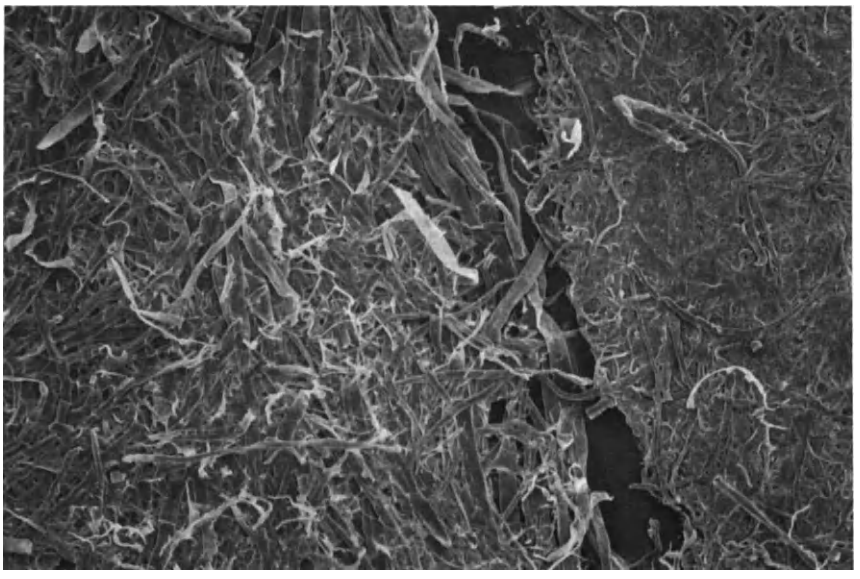


Figure 2.132. A scanning electron micrograph (×45) demonstrating the use of SEM in the solution of leaf-casting problems. Bonding has been rejected along the contact zone, not because the original does not provide the bonding potential, but because of a combination of incompatibility of fibre form and of the mechanical functioning of the leaf-caster. Although the new fibres have orientated themselves randomly in a satisfactory sheet formation in areas not immediately adjacent to the original, the downward draining action of the leaf-caster has caused the softwood fibres to become aligned parallel to the damaged edge of the original, being too long, too large and too unsupple to mesh into maximum contact with it.

of a sheet of paper depends seem to function Chemical degradation of the cell walls and associated physical breakdown of the fibres and sizing materials as well as the 'encrustation' of the fibres by the latter and the degradation products might be thought to inhibit this bonding, but from SEM observations it seems that, at least to a certain extent, there are cementing actions in operation to which these materials contribute.[23]

Beside using the scanning electron microscope as a sort of roving probe with a zoom mechanism to examine a specimen, Polaroid photomicrographs can be taken. To be as useful as possible for later comparative purposes, micrographs should be taken at certain standard magnifications (×100, ×200, ×1000 and ×2000) as well as at magnifications most convenient for the recording of a particular feature. These photographs should go into the albums of specimen sheets of leaf-casting pulps and the photomicrographs taken by transmitted light should go into the files relating to repair of original material so that one can benefit by previous efforts in selecting compatible fibre length, structures etc.

Apart from observing the present condition of the SEM specimens in detail, we can determine and record the effects of their original treatment. Starting with examination at low magnifications we can observe, for instance, how the 'wetter' the furnish is beaten the more the fibres become flattened and ribbon-like, conforming more and more to each other's shape with a reduction in the space of the interstices (this also caused by the progressive development of accumulations of fragments from the cell walls) until it becomes more and more difficult to distinguish their separate three-dimensional nature. Higher magnifications can then be used to examine more closely the actual characteristics and conditions of the fibre walls, particles and fibrillation, etc.

Figures 2.126 — 132 very briefly illustrate some of the range of treatment and condition characteristics that can be observed in single papers as well as bonding zones in aged and weakened papers with leaf-cast lacunae.

Leaf-cast papers produced to controlled and monitored specifications can be photomicrographically recorded in their natural state so that we know that such and such a fibre subjected to such and such a treatment will examine certain diagnostic features. This enables the recognition of similar original manufacturing treatments in artifacts to be conserved as well as facilitating the selection of furnishes and treatments which will result in repairs which both bond and are compatible with them (see Pulp blending below). SEM can thus be used for the cross-referencing or mutual corroboration of two types of intersupporting evidence.

Stock preparation

Internationally accepted standards

In the preparation and beating of pulps, both to produce sheets for experimental purposes and for the repair of original material, a leaf-casting unit should conform to internationally accepted standards[24] for the laboratory preparation and beating of pulps and the forming of handsheets while taking into account the particular restrictions of the conservation discipline. In leaf-casting technology there is an absolute need for precise analysis,

specification and calculation. Mere instinct or unaided visual assessment is not enough to select a compatibly bonding furnish and to calculate the quantity needed for a given area of lacunae. One must be able to consistently control, reliably monitor and quantitatively assess all operations so as to be able to reproduce any characteristics of specimen furnishes and finishing processes. The use of accepted national and international standards provides us with a common language to communicate our findings and to apply the results of work elsewhere carried out to these standards.

Conservation criteria

A leaf-casting unit must conform to conservation criteria in ensuring that its raw materials, fibres and chemicals are of the best, uncontaminated quality and will not contribute to the further degradation of the artifacts under treatment and that they are processed and prepared in correspondingly suitable ways. Although, as has been mentioned above, by careful analysis, treatment and blending of pulps and finishing processes, a leaf-cast paper can be produced whose materials and properties match those of the individual artifact as well as bonding successfully to it, in contrast to the commercial paper-making industry one is greatly hampered in the range of fibres and processing treatments that can be applied in the conservation context. A vast range of potentially useful fibres and furnishes have to be eliminated from one's 'arsenal' because of their inherent chemical instability or by the damage that the preliminary physical or chemical processing has caused in extracting fibres from their vegetable source.

This restriction on our range of raw materials can only be overcome by a great deal of creative ingenuity on the part of the leaf-casting operator in the use of analytical data, the mechanical manipulation and blending of furnishes and finishing processes.

Pulp blending

While the limitations on the exclusive use of dried sheet pulp without further modification and the contribution of beating in the preparation of leaf-casting pulps have been stressed, beating of one fibre type alone cannot produce a paper with an unlimited range of properties. The nature of cellulose fibres is such that the predominance of some properties in the final sheet is possible only by the subordination of others. Thus the properties of folding endurance, bursting strength and abrasion resistance are present in roughly inverse proportion to tearing strength, flexibility, compressibility and opacity. With heavier beating, tensile strength, density and rigidity hardness increase but at the expense of flexibility, compressibility, elasticity and porosity. In the paper industry any one type of fibre or treatment is seldom used alone, but different furnishes are blended to produce a combination of desired properties in the finished sheet whose amalgam could not be found in a paper produced from just one of these pulps and treatments.

The type of fibre itself is important. For example, groundwood and esparto pulps, because of their relatively short fibres, produce papers with some characteristics, e.g. good opacity, bulk and a close even surface, which are much desired in printings. But they lack strength and so are blended with longer-fibred pulps such as chemical wood (which, because of their preparatory treatments, inversely tend to be transparent) which impart better folding and manipulative characteristics.

Much dexterity is required in the balanced exploitation of the inherent characteristics and properties of fibres and those induced in them by preparatory, beating and finishing treatments in order to produce blends with a specific combination of properties.

In leaf-casting we can approach the formulation of repair pulps and papers in two basic ways:

(1) In the case of a recent or earlier paper which is undegraded and does not contain auto-destructive components a bonding furnish can be designed which duplicates the materials and properties of the original producing an entity which, if stored in suitable conditions, will be as chemically stable and durable as time permits. This is relatively straightforward for handmade rag papers, less so for modern papers with highly complex ingredients and a machine 'grain'.

(2) However, in conservation we are usually dealing (particularly in the case of the types of archival and library materials suited to this process) with aged and degraded papers and, as already stated, it certainly would not be ethical and it would be technically ridiculous to produce leaf-cast repairs which duplicated the deteriorated or self-destructive (e.g. groundwood) components of the original.

We thus have the complex task of designing for such papers specifications for repair furnishes and finishing treatments which, although of permanent and durable fibres and other materials different

from those in the present state of the original, yet have compatible physical and visual properties. This is why the author lays particular emphasis on pulp blending and a versatility of stock preparation and analytical equipment and methods co-ordinated with careful analysis of the original material. Even though restricted in the range of fibres we can use, we can still manipulate characteristics and properties inherent or induced in them to produce papers with a broad but controlled range of properties.

Standard fibres

We work with the following range of fibres which we term our *standard fibres:*

(1) Virgin fibres (all carded and combed): first-grade Belgian flax (decorticated to remove shive), hemp, jute.
(2) In sheet pulp form: bleached and unbleached cotton linters (a range of fibres non-refined and pre-refined, from Alpha Cellulose Corporation, Lumberton, North Carolina, USA), PAPRICAN standard bleached and semi-bleached softwood Kraft.
(3) In wet pulp form: western red cedar unbleached Kraft.

(This range will no doubt be extended as experimental work progresses)

Reduction of fibre length

Unlike the fibres in pulpboard form which have already undergone some processing, our virgin fibres flax, hemp and jute must undergo some preparation prior to beating to produce furnishes with characteristics compatible with our original writings and printings. We are mainly concerned with the reduction of fibre length. Although flax pulp is produced in the modern paper industry by a modified Kraft process for various uses such as cigarette papers, Bible and high-quality writings, flax fibres for paper-making in both the hand-made and machine eras have been derived from textiles either worn out from use or from industrial waste. In both instances the fibres have undergone considerable modification during preparation for spinning and weaving or through use. In the handmade era, by the time the fibres reached the beater, the length had been considerably reduced and successive designs of beaters have tended to be based on the assumption that they will be operating with fibres of much shorter length than that of the average virgin flax or hemp base fibre.[25] In the industrial preparation of paper from manila hemp (from old manila rope or waste from the rope manufacture) or jute (from old sacking and string), after cleaning, the fibres are first cut dry to a suitable length. The eleventh century Islamic bookmaking text of Ibn Badis mentions the preparation of paper from flax fibre 'cut... with the scissors little by little'.[26]

We have found using laboratory beaters such as the Valley (although adjustable to perform cutting actions) and the PFI *(see below)* that by the time one has reduced the fibre length sufficiently to conform to the furnish of the original artifact, the pulp is far too wet beaten, producing a paper which shrinks considerably on drying and is especially incompatible with the compressibility of printings.

Therefore to reduce the dry fibres to a more useful length we use a Christy 8 in Laboratory Mill.[27] This is a hammer mill of the overhung cross beater type in which a four-armed steel cross revolves at high speed (8000 rpm) past a curved replaceable metal perforated screen which is situated in the bottom section of the grinding chamber and regulates the size of the finished product which is collected in a cloth bag. The hammering action of the mill tears rather than cuts the fibres fed into it. We use plate screens with 2-3-4 and 6 mm perforations which reduce the fibres to corresponding lengths (it should be noted that the more 'silky' fibres like jute tend to 'ball up' if milled in atmospheres of high RH or if the moisture content of the fibres is too high — it is best to control dry them before milling.)

Preparatory chemical treatment

The cellulose content of flax is approximately 70% with a lignin content of 2-5% together with a varying proportion of non-cellulosic material. Although flax fibres can be prepared prior to beating by alkaline processes such as simple prolonged immersion in quicklime,[28] boiling in solutions of potassium hydroxide, etc., or more complex industrial sulphate processing, the author usually prefers to subject the fibres to a minimum of preparatory treatment, prior to and after beating, as the colour 'toning' properties of unbleached flax are most useful in achieving visually aesthetic infills and linings. Hemp with a cellulose content in the region of 77% is approached in a similar way, although jute with a cellulose content of about 60% contains a significant percentage of lignin and must be initially treated.

Beating

As mentioned above, accepted standards should be followed as far as useful and prudent in leaf-casting. For beating we conform to CPPA Standard C.7, *The Laboratory Processing of Pulp (PFI Mill).* [29] There is a general consensus of specialist opinion that, although each design of laboratory beater has certain commendable features, the PFI mill (*Figure 2.133*) is the best suited for use as a standard apparatus, [30] particularly the latest models. This

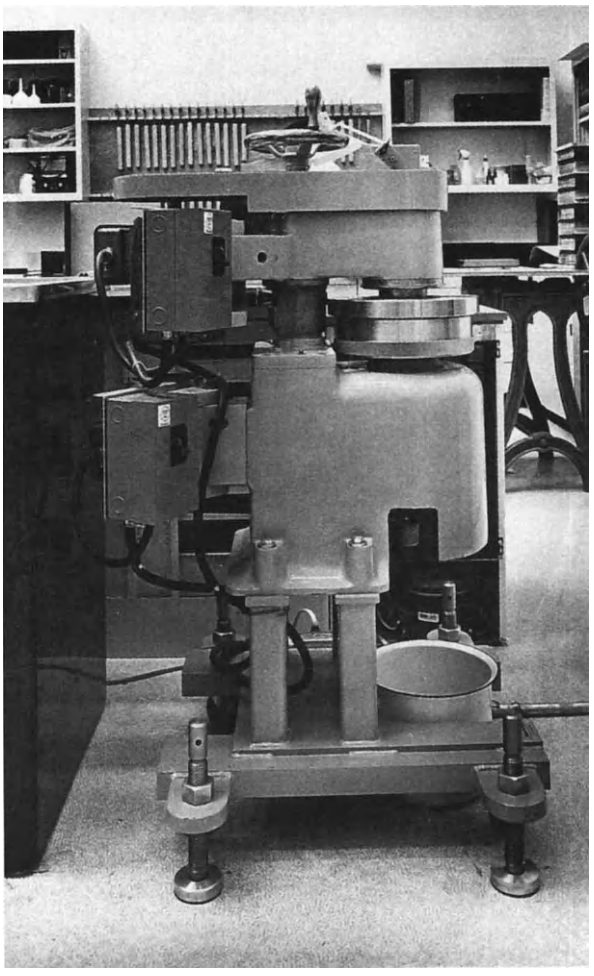


Figure 2.133. PFI beater.

design was developed in the mid-1940s by the Papirindustriens Forskningsinstitut (PFI — the Norwegian Pulp and Paper Research Institute) — in an effort to overcome deficiencies in existing types of laboratory beating apparatus, such as the Lampén, Jokro and Valley, with particular concern for stability (ability to give reproducible results over long periods of time) and ability to work the fibres in such a way that cutting is avoided.

In the PFI mill the variables in the beating process such as pulp consistency, beating pressure and peripheric speed can be varied at will and quite independently. It is a rugged machine, effectively maintenance-free and requires calibration only after major changes have been made to the active components. It is claimed to beat any type of pulp and operate with stock consistencies from 5% to 40%.

The beating elements of the apparatus consist of a roll with chiselled bars and a circular smooth bedplate both made of stainless steel (in recent models). The roll and bedplate are independently driven and rotate in the same direction but the roll has a higher peripheral speed. The unit is equipped with a counter to register the number of roll revolutions during a beating cycle. [31] A predetermined amount of pulp at the selected consistency is placed in the bedplate whose motor is then started and the resulting centrifugal force causes the pulp sample to form an endless band on the inside wall of the bedplate. The roll is lowered into the bedplate and moved towards the inner wall of the bedplate to a preselected gap.

The PFI beater is designed so that the fibres are not cut, the theory being that 'The true potential character of the fibre... can never be revealed correctly during beating if the stress to which the fibre is exposed is not confined to a mere rubbing and pressing... The cutting or severing of the fibres by means of sharp knife edges is at best a question which is connected with the choice of the beating apparatus, and it can never be made the foundation of an analytical method for studying the fibre properties.' [32] The latter is not our principal motive for acquiring a laboratory blender, rather its versatility of operations, and its stability are the major factors in the choice of the PFI mill for the leaf-casting unit. The small quantities of pulp required for leaf-casting can be very quickly and efficiently beaten and its high standards of reproducibility obviate the need for storing special pulps for long periods.

(NB: Since this paper was presented at the Cambridge 1980 conference, a serious problem has been revealed concerning the use of the PFI mill in leaf-casting systems. The beating gap (0.2 mm) recommended in the Canadian Pulp and Paper Association Standard C.7 proved to be inadequate for the beating of cotton. A torque effect was produced which warped the stainless steel shaft at the centre of the beating roll. When this distortion was noticed it was thought that after repair the re-calibration cotton could be beaten at a wider gap, although this would necessitate adjustments in the methods for cross-referencing results with pulps beaten at the 0.2 mm gap. However, further investigation into the problem produced the conclusion that the PFI mill is not suitable for extended use in the beating of linen or cotton or

other non-wood fibres with related beating characteristics (in spite of initial specialist advice to the contrary) and that a Valley-type beater should be utilized if such furnishes are to be prepared.

One of the lessons of this particular experience is that, in attempting to use modern analytical and production equipment for replication of the traditional furnishes of handmade paper prior to the mechanization of paper making, one must take into account the fact that modern techniques, equipment and experience are concerned primarily with the elaboration of fibres and treatments used in the machine-made era and may not always be directly applicable to the esoteric needs of the conservation leaf-casting of historic artifacts.)

It should be noted that a laboratory beater is designed to produce internationally acceptable test data which factor is in some respects incompatible with matching the very varied performance and beating operations of the wide range of beating and refining equipment in today's paper mills. No laboratory mill exists which will replicate all these industrial methods of treating fibres.

Of course, the paper chemist, technologist and conservator have to use laboratory beaters because of their small pulp requirements, as beaters on a commercial scale would in no way be as convenient nor precise, although the latter can do some operations which in the laboratory context have to be carried out using other equipment and methods.

In preparing stock for leaf-casting, besides making maximum use of modern research and technology to produce controllable, monitorable and reproducible results, one must not lose track of the fact that very often we are dealing with early papers and should therefore investigate contemporary accounts (as well as accounts from twentieth century traditional hand paper mills) of the preparation and beating of fibres as well as finishing methods in our quest for sympathetic leaf-cast repairs.

Disintegration

Prior to beating machine dried and pressed sheet pulp or prior to introducing beaten pulp to the leaf-casting chamber these should be disintegrated using a laboratory disintegrator (not 'blended' in a domestic blender) which produces an even dispersion of fibres in water without causing further modification. In disintegrating our stock for testing purposes we follow the relevant parts of the procedure laid down in CPPA Standard C.4. *Forming Handsheets for Physical Tests of Pulp*[33] using a British Standard Disintegrator,[34] (stainless steel, PVC bucket, digital counter) *(Figure 2.134).*

Figure 2.134. British Standard Disintegrator.

At this stage in the equipping of our unit we are not following the next stages in CPPA Standard C.4 for forming handsheets, i.e. sheetmaking, couching, pressing and drying but use the leaf-casting machine (which has been developed from a laboratory sheet former) with hydraulic and manual pressing (*see below*) following our own standardized practice and in stable laboratory conditions as we are particularly concerned with investigating the potential of this individual system.

Freeness

Our pulps are monitored by testing their freeness. This is a measure of the rate at which water drains from a stock suspension through a wire mesh screen or a perforated plate.

It is also known as *slowness* or *wetness,* according to the type of instrument used in its measurement and the method of reporting the results. This drainage rate or freeness is related to the surface

conditions of the fibres and their degree of swelling. It is a most useful index of the amount of mechanical treatment given a pulp both for analytical purposes and for reproducing a given beating regime. It also enables us to gauge the potential of pulp in sheet form as manufacturers usually provide information on the freeness properties of pulps in response to beating expressed in terms of Canadian Standard Freeness or degrees Schopper Riegler.

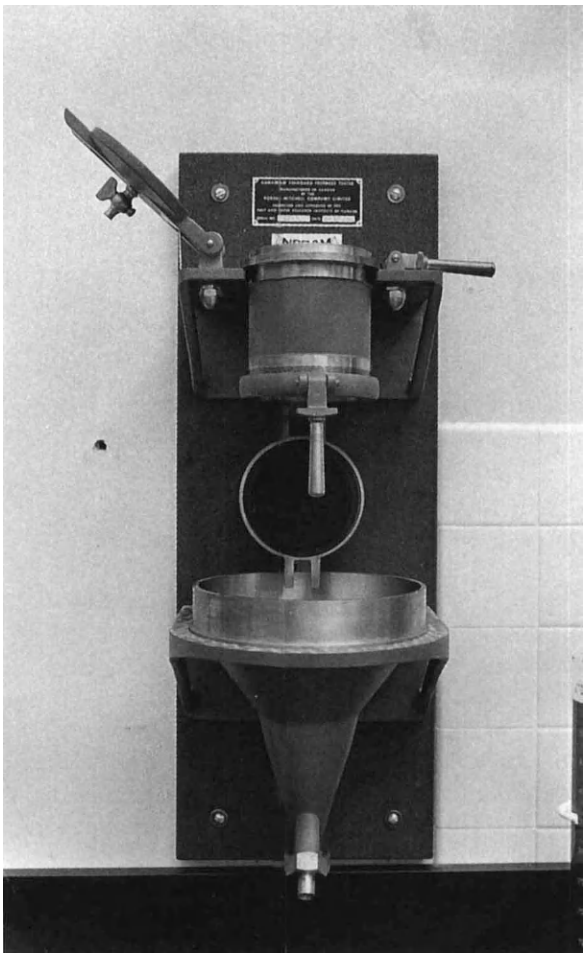


Figure 2.135. Canadian Standard Freeness Tester.

Our choice of the Canadian Standard Freeness Tester was made not only because of the wide use and acceptance of this standard[35] but because of the proximity of the related expertise at the Pulp and Paper Research Institute of Canada in Montreal. The Canadian Standard Freeness test is designed to give a measure of the rate at which a dilute suspension of pulp may be dewatered, expressed in millilitres discharged through the side orifice of the Tester. The relevant standard is CPPA Standard C.1, *The Determination of Freeness*.[36] The procedure was originally designed to yield a test value suitable primarily for the control of manufacture of groundwood pulp but it is also widely used to follow the changes in drainage rate of various chemical pulps during beating and refining (although it should not be used to monitor very wet beaten pulp).

The Canadian Standard Freeness Tester[37] (*Figure 2.135*) is wall mounted and consists of a cylindrical metal drainage chamber, the bottom of which can be closed with a hinged perforated steel plate and lid, both of which can be firmly latched. Below this is situated a rate measuring funnel with bottom and side discharge orifices.

Leaf-casting

We use the Vinyector in place of a Standard Sheet Machine for forming test handsheets. Some minor modifications have been made to this apparatus. The stuff chest in the lower chamber has both hot- and cold-water inlets so that casting can be carried out at higher temperatures. A high pressure spray is positioned above the pulp inlet provided at bench-top level so that any deposits of pulp can be sluiced down before they dry and either clog the pipes or are released as contaminants or unwelcome knots of fibre in later castings. A resilient Neoprene gasket has been fitted around the base of the removable casting screen so as to eliminate leakage of the stock during casting into the lower chamber. At the Spanish National Centre for the Restoration of Books and Documents the Vinyector has evolved to accomodate a recycling of water and residual adhesive between both chambers for efficiency as well as to eliminate wastage of water and adhesive. While the ability to recycle water is an advantage, we do not use aqueous-based adhesives in our system as an economy measure. The precision of measurement of pulp weight and blending proportions means that we cannot afford to have pulp deposited anywhere other than on or in the artifact/s for which it is intended. Any loss of pulp is passed back into the stock to contaminate subsequent castings using different types or qualities of pulp and to increase the weight of the casting. The machine should be adapted to use new water for each filling of the chamber (as does the Israel Recurator).

Reemay spunbonded polyester[38] is the most suitable material the author is aware of on which to cast, possessing a number of advantageous properties. Some of these properties have in recent years made this material almost standard in paper conservation facilities for the support of fragile papers during washing. It is chemically inert: resists mould degradation (therefore can be used again and again), is dimensionally stable in water, (posing a possible

problem in leaf-casting as a casting support as it may not allow the cast paper to dry from its wet, extended state to its original dry dimensions), has a continuous filament structure providing excellent stress distribution (therefore it is able to support fragile paper in water while flexing in tandem with the sheet as it is removed from the water) and has other properties less easy to define such that wet paper will cling to it as it is removed from the washing bath aiding in its safe removal but will not adhere on drying.

As a removable casting screen (casting support) in leaf-casting we also exploit properties for which it is favoured in industrial filtration systems — good filtration characteristics with low pressure drop. This means that if the system is functioning correctly, all fibres introduced into the upper chamber are retained on the surface of the Reemay in the cast areas and are not returned to the chest to pollute the system. The force of the evacuating pump is minimally interfered with by this intervention of a secondary casting screen above the permanent screen. Grade 2014 (first grade) is the one most frequently used for this purpose.

Although it has many advantages it does have another potential disadvantage — new paper cast on to it will take the impression of its surface as a mould mark and, on pressing a leaf-cast artifact during drying, an impression may be left on the original paper. However, the highly dispersed, randomly arranged polyester fibres have a paper-like surface which in fact makes its impression very compatible with non-calendered or non-burnished paper surface relief, including felt impression.[39]

Drying

Other properties make Reemay also useful for drying. It has high bulk and porosity, is 100% polyester and has a moisture pick-up of only 0.5% at 98% RH. It maintains the same level of physical properties either wet or dry and is dimensionally stable during humidity changes. Our drying method exploits this combination of properties.

The wet newly cast sheet is carried on its Reemay casting support to the drying bench and another sheet of Reemay placed on the other side. These are then sandwiched between two sheets of heavy blotting paper either side and pressed. The moisture from the wet sheet passes rapidly through the Reemay to the dry blotters (this effect can be speeded up if the blotters are warmed in a photographic dryer or laminating press). Two changes of blotter at short intervals followed by pressing will leave the newly cast sheet dry enough either to remove from the casting support (still between Reemay) or to be placed between further blotters for transfer to a standing press for complete drying without risk of excess moisture causing distortion whilst drying under pressure.

In producing our basic control and testing samples and in all leaf-casting operations on paper whose extreme degree of degradation means that surface relief characteristics such as type impression have disappeared, the castings are dried in the sandwich just mentioned (between white Formica lined pressing borads) in an adapted hydraulic press,[40] at a standard nip of 60 seconds at 6000 lb/in^2 (incidentally much less than the pressure that can be exerted using a manually operated standing press) followed by a change of blotters and another pressing at the same conditions. The blotters are then changed, this time using lighter-weight smoother blotters (on which is marked a code relating to the casting details) and the pack transferred to a bookbinders standing press for 24 hours after which the castings are removed from the Reemay. The dried papers are stabilized in the controlled environment of the paper conservation laboratory.

Various paper surfaces and type, print and pigment/paint layer impressions or reliefs may require more individual drying treatments, as discussed earlier by Blunn and Petherbridge.[41] The possible application of dielectric moisture profile correction has still to be fully investigated, although consolidation by the application of pressure after sheet forming is a characteristic of all traditional drying methods and would seem to increase the amount of surface area of fibres in contact and hence the bonding area — particularly crucial for successful bonding in the relatively small zone of contact in a leaf-cast artifact.

Specification and calculation

In order to develop dependable criteria for specification and calculation it is essential that the methodological basis for analysis and stock preparation outlined above be extended to encompass these areas, in order to make the routine leaf-casting of artifacts as speedy and reliable as possible. By following the analytical procedures outlined, we can assess the properties of the artifact so that these can be matched, by reference to our repair pulp files, with a bonding pulp producing a paper of corresponding properties after a specified drying and finishing regime. This having been achieved, the amount of pulp needed to cast the lacunae or line the weakened areas must be calculated with

exactitude. With this aim the following programme to assemble data on our standard furnishes has been instituted.

Preparation of samples

Each of our selected fibre sources, be it in the form of virgin fibre such as flax, hemp or jute or as sheet pulpboard, is prepared and beaten to a series of standard formulae defining specified initial average fibre length, beating regimes, etc. and then disintegrated. We then cast for each standard formula or furnish a standard number of 100 cm^2 squares of paper (i.e. each is one hundredth of a square metre) corresponding to substance in grams per square metre (gm^{-2} or gsm) in the range 50—200 gm^{-2} (the range of substances of normal writings and printings) going up the scale in increments of 5 gm^{-2}. That is, from each furnish at the substance values 50, 55, 60, 65, 70, 75, 80, 85 gm^2 etc. we cast 10 samples measuring 10 cm × 10 cm.

Thus 310 samples are cast for each specific furnish. This is a very repetitive procedure and, even working at the maximum production capacity of a leaf-casting unit, it takes at least 2 days to produce all the samples of one furnish (two to four samples are cast at a time). There is a case for casting a smaller range of weights and calculating the caliper of the intervening ones from them, but in the author's experience there is no better way for acquainting oneself with the performance of a given pulp during casting and drying operations than by going through the whole routine. It is an ideal discipline for the initial stages in training in leaf-casting. The number of samples produced also provides sufficient material for physical-strength testing (although for these purposes larger sheets may have to be cast to produce the necessary size of samples required by some testing standards). The assembling of the large body material necessary for comprehensive testings to be carried out could be shared between a number of different leaf-casting units if a standard methodology was agreed.

After casting, these samples are pressed and dried according to the standard procedure outlined above. Further series could be produced and finished to give various calendered or burnished surfaces.

The same procedures are carried out for blends of pulps each prepared to the standard formulas.

After drying, the sample squares are then removed from the casting support material and details of treatment recorded in pencil on each one. They are then left to stabilize in the laboratory atmosphere. The caliper of each sample is then measured with a paper micrometer at the centre and 25 mm diagonally in from the corners of the square and each reading recording in a specially prepared table. An average is then taken of these readings and recorded in an adjacent column. The overall average is estimated from the ten individual samples of each substance and listed in a separate column. Therefore we know that a specific weight cast in a specific area (a specific substance) of a specific furnish dried and finished in a specific way has a certain average caliper. After these measurements each sheet is then oven-dried in a microwave oven and weighed on a digital balance to 0.001 g. This figure can then be compared with the original oven-dry weight cast in order to keep track of any pulp loss or other irregularity in machine operation.

(Since this paper was presented at the Cambridge 1980 conference and following the success of the computer measuring system mentioned below it was thought useful to investigate the possibilities of a computer plotting system to transfer or transfer the calculation tables into graph form. This would enable easier reference and also would indicate all substance and caliper values in the range selected rather than relate solely to increments of 10 gm^{-2}. Under the guidance of Ray Lafontaine, Chief, Environment and Deterioration Research Division of the Canadian Conservation Institute, a Hewlett Packard 9866A Printer and 9862A Calculator Plotter were successfully used with a Hewlett Packard Pac 3 (Polynomial Regression) Program. Graphs were thus produced from the data noted on the recording and reference charts of paper sample measurement (see Figure 2.136). This system offers great further potential in that it may eliminate the need to carefully grade the increments or paper control sample substance cast (50, 55, 60 and 65 gm^{-2}, see above) which has been the most convenient way to produce calculation tables. Instead, it may be possible to simplify matters by casting for each furnish a group (of large enough a number and substance range to provide useful statistical data) of samples of constant area but random dry weight, and from their measurements of area, weight and average caliper to computer plot a graph from which intermediate values can easily be read. An extra advantage of the computer plotting system is the ability to generate a mathematical assessment of the consistency of the relationship (coefficient of variability) between the substance/caliper values and the dry weight values of the control sample sheets.)

Thus having selected a sample paper a particular leaf-casting furnish and finishing treatment which would be compatible with the paper of a given artifact, by reference to these prepared tables or

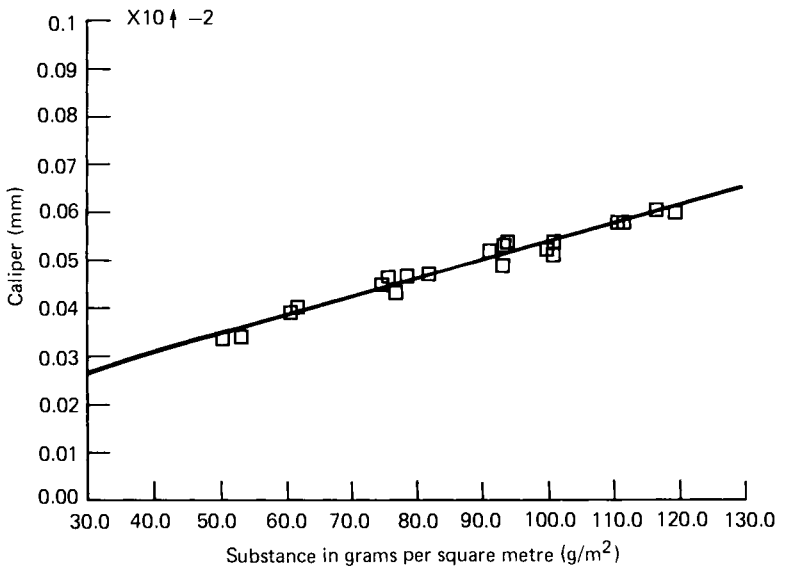


Figure 2.136

computer generated graphs we can easily find what substances to cast just by measuring the caliper of the original artifact. It is then left to calculate the area we need to cast.

Calculation of area

Knowing the caliper of our original leaf (or, in the case of casting a lining, having chosen its caliper) and having chosen a compatible furnish and treatments which will produce a compatible paper, whose substance in grams per square metre is known, and finishing processes, the metric area to be cast must be measured.

At CCI the author has designed a light table for leaf-casting measurement with a hand-guided tracer point. The light table (*Figure 2.137*) is a modification of the type in general use for paper sub-illumination but, instead of having a single glass sheet as its working surface, it has two sheets one above the other and hinged along the back edge so that the upper sheet can be opened back. The lower sheet is of ¼ in. thick clear safety glass on the underside of which is silk screened a 1 cm grid of fine black lines (a second sheet with a 10 cm grid is also used and can be interchanged with the first). The upper sheet is not made of glass but of ⅛ in. thick clear polycarbonate. This material is preferable to glass for this purpose. It is safer as it will not break so easily and cut. It is strong and fairly flexible and is less susceptible to scratching than Perspex or Plexiglas.

When measuring a paper leaf, the upper polycarbonate sheet is opened back and the leaf is positioned on the lower glass. The grid allows exact alignment, for example, of fragments or two separated leaves of a bifolio and the desired perimeter of the actual casting can be marked out on it. This may be the original outer dimensions of the leaf or sheet or can allow for an extra trimming or binding margin (I mark out the corners with red Letraline tape (*see Figure 2.137*)). When aligned correctly the upper polycarbonate sheet is lowered and holds the paper in place and protects it during measurement. Polycarbonate such as Perspex and Plexiglas is subject to static charge, but this is an advantage here as it helps to keep a fragile leaf, often in many fragments, in place.

Fully automatic instrumentation for the measurement of areas in leaf-casting has yet to be developed, although some experimentation with light-scanning techniques has been initiated and it is probably just a question of putting the necessary finance and specialist knowledge together to solve the problem. Planimeters have been used by a number of units.

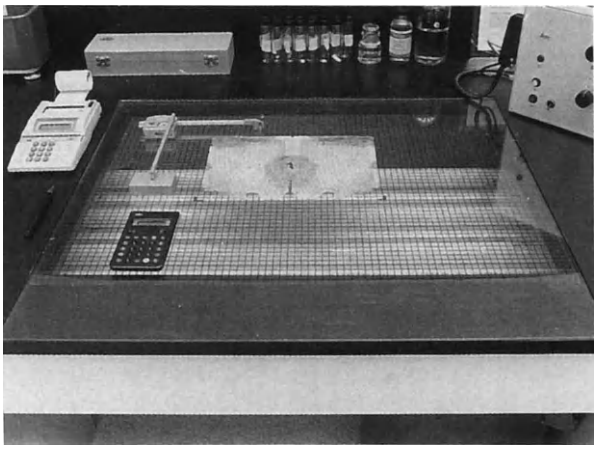


Figure 2.137. Light table designed for leaf-casting calculations. Note planimeter.

In our unit a compensating polar planimeter is used. This is the most widely used type of integrator due to its versatiity and the simplicity of its operation. Areas are measured with planimeter by simply

guiding the tracer point once around the boundary of the area to be determined. For leaf-casting measurement the planimeter must be large enough so that it can circumscribe the type of areas that one would expect to cast. A planimeter with a fixed tracer arm is sufficient as the vernier reading (a vernier value of 10 mm^2 is required) must indicate directly the metric area without recourse to conversion tables. It must, however, be equipped with a zeroing device which permits the measuring wheel and the dial to be zeroed by simply pushing a knob. The result of the measurement can thus be read off immediately without calculating the difference between the initial and final readings. It should be equipped with a tracer point, rather than a tracer lens, as this makes it easier to trace the often complex configurations of lacunae in paper artifacts.

At CCI we are now beginning to use a computer system (Hewlett Packard Digitizer) which, although requiring hand tracing of the areas to be measured, automatically computes the area. Like the planimeter, it is subject to human error in the exact outlining of areas but offers much promise and is more convenient to use (*Figure 2.138*).

Figure 2.138

Summary

The leaf-casting process offers great potential for the repair of a wide range of damaged paper artifacts, some of which cannot be satisfactorily restored by any other method. The soundness of the basic concept has been demonstrated by results, in the form of the leaf-cast papers themselves, and corroborated by SEM investigations into the bonding of leaf-cast to original fibres.

Just as in hand paper making the vat/vatman (and in machine paper making, the sheet-forming machine) is only one component of a manufacturing system, so a leaf-caster itself can only function successfully as one part of a system, based on a knowledge of the raw materials of paper making, their responses to treatment, the characteristics and properties of pulp and paper at both the microscopic and macroscopic levels (including after ageing) of which analysis (using resources within and external to the leaf-casting unit), stock preparation, drying, finishing equipment and specialist operators are the other components. The precision analysis, specification and calculation required in order to produce repairs compatible with the immense range of historical papers imposes strict methodological requirements. It is hoped that the present paper will help in this realization.

Notes and References

1. The only previously published study describing a complete system is that of two workers at the M.E. Saltykov-Shchedrin State Public Library in Leningrad, Nyuksha, Yu.P. and Blank, M. G. (1976). *Potochnaya Liniya Dlya Restavratsii Knig* (A Flow Line for the Restoration of Books), Moscow (in Russian), which testifies to the seriousness with which they approach their subject (although there is a reliance on adhesive technology and on drying techniques and apparatus which may affect important inherent characteristics of printed papers such as paper surface texture, type impression, etc.). Perkinson, R. and Futernick, R., (1977) in 'Questions concerning the design of paper pulp for repairing art on paper', in *Preservation of Paper and Textiles of Historic and Artistic Value,* Williams, J. C. (Ed.), Washington, D.C., 86-94, have briefly examined the question of pulp specification for infill repairs on works of art on paper. Since the Cambridge 1980 Conference the results of some preliminary work by Per M. Laursen, 'Untersuchung der Fasern zur Papieranfaserung', were presented to the "5. Internationaler Graphischer Restaurorentag" held in the Hague, 12-16 September 1983.
2. For bibliographies see: Blunn, D. and Petherbridge, G. (1976). 'Leaf-casting — The mechanical repair of paper artifacts', *The Paper Conservator,* **1**, 31-32 and Laursen, P. M. (1983). *Description of Various Fibre Bonding Apparatus,* Humblebaek (in Danish).
3. Haupt, W. (1976). 'Möglichkeiten und Grenzen der partiellen Papieranfaserung im Spritzendruckverfahren', *Maltechnik,* **82**, No. 3, 198-203.
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7. Nyuksha and Blank (1976), *op. cit.*, Nyuksha, Yu.P. and Blank, M. G., (1975). 'Restoration of paper with paper pulp containing polyvinyl alcohol fibres', Preprints, ICOM Committee for Conservation, 4th Triennial Meeting, Venice, No. 75/15/13-1-10; (1958). 'Application of paper pulp in restoration work', *Restavraciya Bibliotechnykh Materialov*, Saltykov-Schedrin State Public Library, Leningrad, 41-48 (in Russian); (1975). 'The technology of conservation and restoration of library materials', *Restaurator*, 2, No. 2, 65-79. Belen'kaya, N. G., (1964), 'Methods of restoration of books and documents', in *New Methods for the Restoration and Preservation of Documents and Books* (Novye Metody Restavratsii Knig), National Technical Information Service, TT-64-11054, Jerusalem, 22-49.
8. A terminological distinction perhaps should be made between **pulp infilling**, whether manual (see Keyes, K. Mizushima (1976). 'A manual method of paper pulp application in the conservation of works of art on paper', *The Paper Conservator*, **1**, 33-34) or mechanical (see Futernick, R., (1983). 'Leaf-casting on the suction table', *Journal of the American Institute for Conservation*, 22, No. 2, Spring, 82-91), where the visual result in an artifact which will remain essentially in one plane is of primary importance (e.g., in works of art on paper) and which does not necessitate elaborate systems of pulp preparation (and where bonding can be assisted by the introduction of adhesives) and **leaf-casting** which aims, through a complex system of paper analysis, pulp specification, preparation, calculation and paper finishing mechanisms, to achieve optimally integrated fibre bonding at the old/new paper interface (without unwarranted resort to adhesives) and compatible manipulative and dimensional stability properties across the entire leaf — so essential for most library and archive papers.
9. Nyuksha and Blank (1975), *op. cit.*, Nyuksha and Blank (1976), *op. cit.*, 21, 33, 34, 39.
10. *"Kuralon" for Paper and Non-Woven Fabrics*, Kurasay Co. Ltd., Osaka (n.d.) *"Kuralon VP" (Polyvinyl Alcohol Fiber) and "Eaglets SCR" (Short Cut Rayon) for Paper Making, Technical Instructions*, Kurasay Co. Ltd., Osaka (n.d.).
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18. Norris (1965), *op. cit.*
19. Sartorius Series 1200MP electronic balance with push-button taring and 0.001 readability.
20. Norris, F. H. (1952). *Paper and Papermaking,* London, 68. See also Clark, J. d'A., (1978). *Pulp Technology and Treatment for Paper,* San Francisco, for an extremely informative treatment of this and related subjects. Clark stresses that contrary to much of the literature, shortening of fibres by extensive beating per se does not appreciably decrease the freeness of drainage quality of pulp. The observed decrease in freeness is caused mainly by the concurrent production of additional debris and to a lesser extent by fibiliation.
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35. Clark (1978), *op. cit.,* 279, is in extreme disagreement with the customary point of view here, "All pulps contain various percentages of fine particles, usually termed debris, which increase along with other

changes in beating..... Unfortunately, because debris sensitively restricts the passage of water through a thick mat of pulp, the quantity of debris produced, measured indirectly by means of a freeness tester, is presently widely chosen as a valid measure of the degree of beating..... In fact, freeness is a poor and often completely misleading measure of ... these effects".

36. *The Determination of Freeness,* Standard C.1. Prepared by the Physical Standards Committee Technical Section of the Canadian Pulp and Paper Association, Approved Method (October 1940), Revised (1952) (1962) (1967) (1969) and (April 1972).
37. Manufactured by Robert Mitchell Co., Montreal, Quebec, Canada, and calibrated by the Pulp and Paper Research Institute of Canada Physical Analysis Section.
38. Manufactured by Textile Fibers Department, Spunbonded Products, E.I. du Pont de Nemours and Co. (Inc.), Wilmington, Delaware 19898, U.S.A. For technical information consult *Properties and Processing of Reemay, Spunbonded Polyester Bulletin S-13, (August 1974).*
39. Reemay can be mechanically finished at increased temperatures and pressures to achieve smooth surfaces but this reduces the porosity and possibly its usefulness as a filter and drying material for leaf-casting purposes. While on the subject of casting supports and surface impressions it should be noted that Robert Futernick has recently published an admirable paper, (1983). 'Leaf-casting on the suction table', *Journal of the American Institute for Conservation,* **22**, No. 2, Spring, 82-91, which includes a description of an innovative method of producing a leaf-casting screen replicating the effect of laid wires with a silk screen imaging system using a photosensitive emulsion on a plastic support.
40. Earlline Hydraulic Standard Press Model ES-200, manufactured by Earll Manufacturing Co., Minneapolis, U.S.A., to which a reinforced plywood nipping table has been added with a polished serpentine lower platen so that any moisture from pressing wet paper will not cause corrosion — and for possible applications in glaze-drying under pressure.
41. Blunn and Petherbridge (1967), *op. cit.*.

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3.1
Repair and Relaxation

3.1.1 Repair treatments for vellum manuscripts

Anthony Cains

The Methods described are those used for the repair of vellum manuscripts at Trinity College Library Conservation Laboratory, Dublin. Meticulousness is emphasised in the documentation of each leaf and its relation to the structure of the volume of which it forms part. The hydration and tensioning of damaged and distorted skins are described using methods related to the original parchment making process, rather than by applying pressure. Instructions for the preparation of repair materials, including skin, adhesive systems and supports are given as well as repair techniques such as infilling, overlaying lacing and guarding — with accompanying diagrams. The resewing and conservation binding of vellum manuscripts are briefly addressed as is the subject of suitable cases for exhibition and transport. Illustrated information is provided regarding the manufacture of the necessary specialised repair tools and the acquisition of repair materials. An appendix is included on the dyeing of vellum.

Reed informs us that vellum is a network of protein fibre (collagen) under tension in a matrix of a ground substance of a mucous type secretion (muco-polysaccharides) with high water-binding capacity; and that the tightness of the fibre network varies with, for example, the flanks and belly loose and the spine area compact. On the character or nature of the material he says:

. . . 'the essence of the parchment process, which subjects this system of pelt to the simultaneous action of stretching and drying, is to bring about peculiar changes quite different from those applying when making leather. These are: (1) re-organization of the dermal fibre network by stretching and (2) permanently setting this new and highly stretched form of fibre network by drying the pelt fluid to a hard glue-like consistency. In other words, the pelt fibres are fixed in a stretched condition so that they cannot revert to their original relaxed state.'

Our method of repair at the conservation laboratory, Trinity College Library, Dublin, aims to preserve the original character of the material by using methods related to the parchment making process, in particular by our emphasis on hydration and tensioning. Pressure methods will not do this nearly as well. Change or loss of this original stressed condition brought about by changes in relative humidity or accidental wetting is best corrected by this ancient method (when the physical condition of the material allows), in conjunction with a stable and correctly balanced storage environment.

Documentation

Roger Powell's chapter in Philip Smith's book *New Directions in Bookbinding*[2] contains important advice on documentation. The author strongly recommends that one uses a low-power binocular microscope ($\times 10$—$\times 80$) to examine the manuscript and to record such detail as fine debris (silk fragments from endbands, detached pigment, mould debris and soil and other inclusions to be removed); hair follicle pattern/grain to determine spine direction; hair side and other surface features

that could be of value in determining the original collation; conjoint bifolia; species of animal; condition of pigment and its stability and so on.

During the subsequent repair work a microscope is invaluable for such operations as removal of old adhesive without disturbing the surface of the subject; separation of blocked material; cleaning the non-image areas of the skin (of dried mould or insect debris); and fixing pigment.

In the case of the *Book of Mulling,* repaired in the last century, the restorer had inset each leaf into a thick paper panel. On sanding the scarfed join he also removed rubrication and scratched the surface of the vellum. To the naked eye the damage seems slight but under the microscope one can really understand how massive the damage is in relationship to the size of the leaf.

In addition one may study the nature of cuts, score marks and perforations of various forms (which can be another useful aid in determining the original collation) and an immense amount of detail not easily visible to the naked eye. As an aid to accurate recording and safe precise repair this instrument is indispensible. The addition of photomicrographic processes provides an important means of recording the condition of the manuscript. To give a contemporary example, the series of transparencies taken during a recent exhibition of early Irish manuscripts in the United States were examined (and compared with control transparencies) under the microscope to monitor the stability of the pigment during the course of the exhibition. (It must be remembered, however, that variations in lighting conditions, processing and the effects of age can affect the colour of transparencies and thus the extent to which those taken and processed at different times can be effectively compared.)

In addition to photography and detailed notes, we take a tracing of each leaf recording the shape and location of all features except the image itself *(Fig. 3.6).* The design of the infilling, guarding, sewing or thonging and transparent membrane overlays and flanges are drawn as an exact guide to each of possibly several hands who may deal with the one manuscript. Also indication is given of the tone, type and thickness of the repair material. By such means control is maintained by one person. The tracing is, generally speaking, only necessary for a manuscript that has been reduced to single leaves during previous restoration or is extensively damaged or composed of separate fragments. The tracing is made after the first flattening, but if many fragments have to be separated, tracings are taken before and during the process of removing the old repair patches or separation of the blocked leaves. To tie in the details recorded on the tracings with the written notes a grid reference system is used. We have constructed a frame of card on which are tensioned bisecting threads set at one-centimetre intervals. Where two threads cross to form a precise grid a touch of glue was applied to keep them in register. Ruled plastic film could also be used. The thickness of the leaf can be gauged and the reference points noted on the tracing or in the accompanying notes. This gauging can be useful in identifying original conjoint bifolia — along with other evidence such as scraper or tool marks, grain pattern, etc. The gauging marked on the tracing is a guide to the weight of the repair materials that will be needed and is another aid to co-ordinated planning of the repair work. Each repair component should have a specific function. The inlays, sewing laces and guard should be designed with care and applied with due consideration to the final appearance, function and use to which the material will be subject. It is not necessary to mend every hole or tear and one should resist the urge to do so without good reason.

Hydration

Even with the greatest care some alteration to the appearance, the opacity and surface texture of the skin may occur during the process of hydration and flattening. This will be particularly noticeable when only part of a manuscript is treated. The type of material most vulnerable to this change is the later manuscript vellum of Western European manuscripts of the fourteenth to sixteenth centuries, the surface of which has received a vigorous surface dressing to a point where the follicle pattern has lost its definition. Probably the torn surface fibres congeal or gelatinize more readily than the relatively smooth surface of the undressed material and are consequently changed. We have dealt largely with previously restored or mould and water damaged material where the opacity and surface texture are now far less sensitive. We would suggest that material in fine original condition but thought to be in need of flattening be hydrated/conditioned by the humidity chamber method only, at the lowest moisture content sufficient to make the material pliable and flattened by a fast clip and pin operation or by light pressing. (Our humidity cabinet is used for relaxing folded or very distorted documents as the initial treatment and for the humidification of illuminated folios and the final conditioning and flattening of repaired material. The high relative humidity of the chamber (85-95%) is maintained by an evaporative (not centrifugal) type domestic humidifier. The process is so slow that the degree of hydration can be controlled

exactly to give a moisture content of 22-28% for initial tensioning and flattening, and 15-20% for final flattening after repair.) A work room RH, of 65—70% would help a lot because the skin could be hydrated to a precise point without having to allow for loss by evaporation during the pinning out operation before the leaf is under controlled restraint. The removal of spine adhesive and subsequent binding by a non-adhesive method will do much to improve the condition of the manuscript if it is subsequently stored at a stable RH of 60% or slightly more. The advantage of flattening vellum can be largely negated by dry storage or exhibition. The advantages of a flat and moisture-conditioned membrane manuscript are: good opening and flexing of the leaves and consequently a reduction in localized abrasion and pigment loss; the pigment binding medium remains flexible (having been consolidated and its stability improved by hydration); the solidity of the text block inhibits the entry of dust; will allow more precise photography and less risk of damage; and permits precise repairs and binding.

The skin can be humidified by water vapour derived from a damp pack of fabric or waterleaf paper through a permeable barrier of several layers of polyester web. The moisture content of the pack is controlled as is the time of exposure to the water vapour. Moisture content can be maintained by immersing the fabric or paper in water and then interleaving with similar but dry material in various proportions and finally pressing to distribute the water evenly through the pack. Moisture content can be confirmed by the weighing and drying method or more conveniently by using a moisture meter.

When free water is seen to have moved to the surface of the polyester web next to the manuscript, change it for dry material. As a precaution one may change the web each time a leaf is inserted. The damp pack can take the form of a flat pack of interleaved material taking one or several manuscript leaves at a time or a cylinder for single, usually large skins. The cylinder we use is a plastic pipe 100 mm ϕ with a moisture reservoir of linen and several layers of polyester web covered finally in a sheet of polyester film or polyethylene. The advantage of the cylinder is that the action of rolling compels the skin to conform without excessive pressure. Raise the ends of the cylinder so that the weight is taken off the subject, or tie and stand the cylinder on end.

In the flattening procedure with the interleaving method, the work cycle is balanced so that each bifolio or leaf is in the humidity pack no longer than necessary for it to become pliable. Start with two or three leaves in a pack capacity of ,say, six leaves. As soon as the first is ready for tensioning, place another in the pack. The timing should be such that the 'tensioning' and associated operations equal the optimum period of exposure to humidity.

The complete sequence is:

1. Humidify the skin.
2. Set clips (over folds of blotting paper).
3. Tension.
4. Drying period.
5. Release — placing clips and pins down neatly for next leaf.
6. Interleave between dried double layer blotting paper and polyester web (no watermarks or colour).
7. Press between formica-lined pressing boards.
8. Pressure only sufficient to counter resistance of vellum — use weights but not screw pressure.

The humidity of the damp pack should be adjusted to suit the gauge and type of skin as well as the timing of the process (given that one is also concerned with productivity and even processing results). Skin with very irregular gauge or less absorbent or horny zones can have local treatment with ethanol and water or isopropanol/water solutions. The advantage of the chamber method is that the hydration process is slow and one can determine the best conditioning point within a broad time scale, whereas with the pack system seconds can be important, particularly on thin material.

The flat pack method is not suitable for the initial flattening of severely distorted vellum for which the chamber or solvent systems would be better (or a 'cylinder-pack' can be tried). Shrunken material that does not respond to these hydration and flattening methods will probably require the Belaya urea treatment [3] of which the author has no experience — but understands that it works wonders.

In separating blocked water and mould damaged skin, the water/propan-2-ol/ethanol[4] solutions have proved useful for controlled local dampening and manipulation of distorted areas of skin and the removal of adhesive and the separation of blocked leaves and fragments under the binocular microscope. Immediately a fragment is detached its shape and exact location is recorded either by tracing or sketching and appropriate notes. Whilst the fragment is damp, do as much cleaning work as possible (that is, removing softened glue and decay debris) and then leave to dry between polyester web and blotting paper. (Beware offsetting of painted or written areas — see below.)

When dry and flat, the fragment is kept in a polythene envelope along with its tracing. We must emphasize the importance of adopting a system that

identifies each component and the location from which it was removed.

Tensioning

The tensioning operation is not without its dangers to the novice. Poorly modified clips combined with excessively high moisture content in the vellum will produce indelible marks along the margin. Furthermore, the relaxed condition of the skin encourages overstretching.

Tensioning should not be so strong as to remove all the distortion initially; the clips must only restrain the skin while it is drying until the moment of reaching equilibrium when the skin comes under tension and is more or less flat. It is better to stage the flattening of very shrunk or distorted material, gradually improving its shape — given that it is not so degraded as to resist the treatment and require another approach.

The clips are arranged neatly on the soft insulating board with folds of blotting paper and needle awls to hand. There should be sufficient clips to cover the entire edge of the bifolium or leaf. The subject is placed centrally on the board and immediately one starts to hook the blotting paper guards (NB: there is no advantage in fixing the folds of blotting paper to the rubber packed clips) on the edge (5 mm wide fold to the edge), and place each clip in alignment with the inside edge of the guard, placed at intervals of no more than 5 mm. For large skins the assistance of a colleague may be necessary, depending on the moisture content and RH of the work room. When tensioning we find it is best to hold an awl in each hand placing the point through the lower plate of the clip immediately opposite one another and pinning down simultaneously. When all have been secured to the deck, adjustment of individual clips can be made to give the balanced overall tension. One is tensioning, not stretching, the skin — the effort must be slight.

Small tears can be temporarily reinforced with Scotch tape (transparent pressure-sensitive tape) for the initial flattening. When placing the skin on the fibre deck, have the spine fold uppermost, if possible, so that when it has been tensioned, softened glue can be scraped away with a sharp folder. If the skin curls towards the hairside rather excessively, then place the hair side down to facilitate the placing of the clips — and reduce the exposure time to water vapour of the remaining leaves in the pack. Allow the skin to dry to a lower moisture content before tensioning. When tensioning material with unequal margins, pay particular attention to the original ruling and margin marks as a guide.

We generally prefer to remove the leaf from the clips before it is completely dry. When the surface is dry to the touch it is removed from the deck (and any pressure-sensitive tape supports removed) and placed between polyester webs, blotting paper and pressing boards. The blotting paper is subsequently changed several times until the subject is in equilibrium with the workshop RH, with an EMC (Equilibrium Moisture Content) of about 10%. Care must be taken to avoid damage to the image. The polyester prevents set-off, but in the pack hydration method set-off can happen if the membrane or the polyester web is allowed to become too damp. As a precaution, small zones of vulnerable pigment or gilding can be insulated from the moisture by applying masks of polyester film or polythene or even silicone paper.

Loss of pigment due to set-off onto damp interleaving must be avoided at all costs. Decayed material, fragmented, or otherwise lacking tensile strength, must be flattened initially by pressure. Flat paper-lined weights sufficient to cover the entire leaf should be prepared. Sections of cold rolled mild steel are ideal. The leaf is hydrated just to the point at which it becomes pliable and then manipulated carefully to ease out the more pronounced creases. The spine fold is the usual area requiring such 'assistance'. Of course, one must avoid contact with the softened image. The leaf is placed on a base of polyester web and blotting paper with several layers of polyester web on top. The weights are then placed on the leaf, sliding them from the centre to the edges, gradually easing out the creases and covering the entire leaf. After a drying/setting period of, say, 10 minutes the weights are removed to be replaced by blotting paper and a pressing board. If the distortion is slight the fragile skin can be hydrated just sufficiently to relax and then interleaved and placed between pressing boards to dry (see below for further details).

Repair

Our system of repair requires the use of the following materials (see below for further details):

1. Calf slunk.
2. Undressed gold-beater's skin.
3. Edible gelatine.
4. Acetic acid.
5. Sorbitol.[5]
6. Heat-set tissue.
7. Bayer and ICI aniline dyestuff.
8. Photographic blotting paper.
9. Bondina polyester web.

Materials preparation

The transparent membrane (gold-beater's skin) is prepared by 'degreasing' in a bath of acetone followed by a thorough pouncing with pumice powder on both sides and then mounted onto our laboratory prepared heat-set tissue[6] which renders it completely manageable. The temperature currently favoured is 60°C at a pressure of 40 atmospheres and a dwell of 20 seconds. In use, the humidity of the gelatine adhesive (see below) allows the stabilizing tissue to be easily removed.

The calf slunk is prepared — if necessary — by sanding, pouncing, scraping/shaving, and surface staining (toned with water-soluble aniline dye).

In scraping, a rectangle of about a square foot in area is cut from the skin and 'Scotch taped' along its entire edge to a plate glass surface over a light box. The scraper used is a very sharp (Arkansas stone finish) spoke-shave blade (Stanley for preference — or one made from cast steel or high-speed steel) with a slightly curved cutting edge as for paring leather. A turned (burred) scraper edge is not suitable for this work.

The light box allows the gauge to be judged during the course of the work. To avoid tears as the skin becomes thin — particularly if you need to produce a transparent piece or area for direct overlaying of the infill — one must reduce pressure and keep the knife sharp. In this way the skin can be made more uniform in thickness thus enabling one to use all the skin or to modify an inlay/overlay to have the right gauge at the right point. Results are superior to mechanical or hand sanding and control more precise. *(Figure 3.1).*

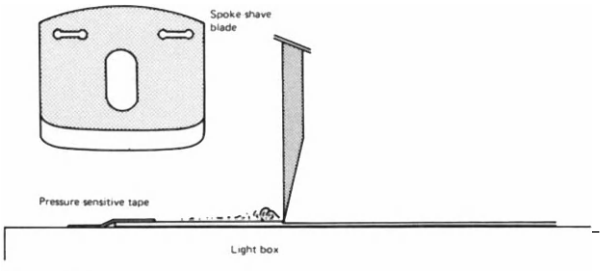

Figure 3.1.

The infill should never be thicker or more rigid than the subject. Scraping is always from the flesh side but the hair side may be lightly sanded or pounced to give a texture similar to the subject and this also aids the even staining of the surface.

At present we prefer to use edible leaf gelatine as an adhesive (12% w/v to which is added the humictant Sorbitol). We have used PVA very successfully in the past, but an internally plasticized type giving a hard but flexible film. The amount one uses and its precise control is critical for good work. The worst example that comes to mind was one where a vellum manuscript had been repaired with an over-plasticized PVA emulsion that struck through the vellum, causing wax-like stains; the adhesive crept beyond the contour of the repair to which dust adhered, and the leaves blocked.

Repair methods

1. Guarding with scarfed vellum — glued and laced *(Figure 3.2).*

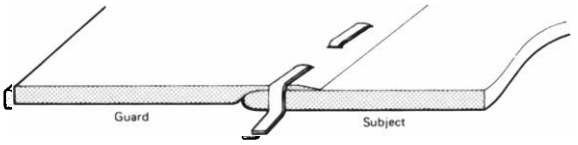

Figure 3.2.

2. Throw-out guards.
3. Infilling with broadly scarfed vellum overlaid onto subject.
4. Infilling with narrowly scarfed vellum onto a flange of transparent membrane *(Figures 3.3* and *3.4).*

Figure 3.3.

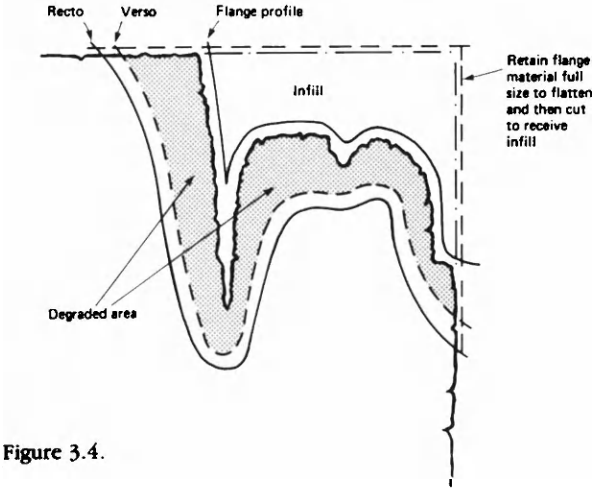

Figure 3.4.

5. Infilling combining both methods.
6. Infilling with transparent membrane.
7. Overlaying — reinforcing with transparent membrane.
8. Overlaying and infilling in one piece with vellum made transparent in defined areas by scraping.
9. Lacing and sewing guards, infill and tears and securing original vellum-maker's repairs. *(Figure 3.5).*

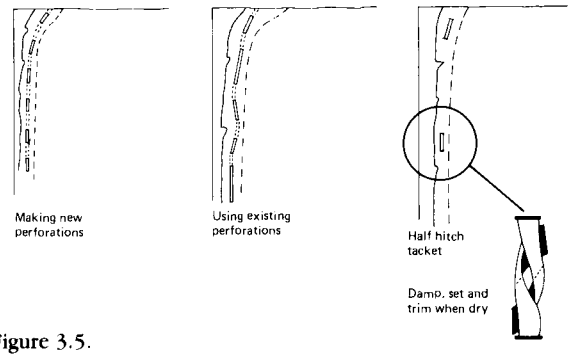

Figure 3.5.

For valuable or extensively damaged material the repair work can be planned and defined in the tracing. Naturally, such preparation is necessary only for a small proportion of the material we handle and is generally used for the part of a manuscript requiring such control.

Notes on repair methods listed above

1. The vellum should be thinner and more flexible than the subject and broadly scarfed. The contour should not be completely parallel but open out at the head and tail to give a wedge-shaped form which provides a greater area of adhesion and makes for a better flexing 'transition' at these vulnerable points. *(Figure 3.2).*
2. For the manuscripts that require a new binding and are now composed of single leaves some extra width can be added in the spine margin, but this should be kept to the minimum. It is not always practical to reconstitute the original gathering structures as the gatherings were often extremely thick. On the back board of the new binding or protective case a collation map should be preserved indicating the originally conjoint bifolio. This map is based only on the evidence of careful examination under the binocular microscope and will be of assistance to scholars in determining the original collation of the manuscript.
3. Given that the repair is necessary for the support and protection of the leaf a patch is cut from the prepared and toned slunk. The shape is outlined on the flesh side giving the overlap profile and the contour of the subject. The width of the pared overlap, between 3 and 5 mm, is kept generally parallel but may be narrowed to avoid text or widened to give extra local support.
4. The flange is built from three stepped layers of transparent membrane. The first layer of heat-set tissue supported membrane is cut and scarfed with sanding sticks[7] and fixed. The glue is applied in stages to avoid chilling — (the warmth of our light boxes helps) — not terribly efficient but a useful defect in this context. All pencil marks are made on the tissue side. The middle layer is cut to about the edge of the subject and when fixed the support tissue is pulled away. The third layer is prepared and attached at the first but not in exact alignment with it. The leaf is conditioned in the chamber and flattened. When air dry the profile of the flange is cut to give a clear parallel contour about 3 mm at the narrowest point. A patch of vellum is then prepared to fit onto the flange.
5. You may prefer to restrict the flange method to text areas only and overlay blank portions.
6. The build up of the middle layers of transparent membrane can be such as to form a useful infill for relatively small lacunae.
7. Overlaying perforated text with transparent membrane is a simple matter with heat-set tissue-supported material. Avoid overlaying thick water-soluble pigment if possible but this is not imperative — just be careful and press into contact with fingers only. Generally speaking, it is better to apply the membrane to the hair side only, particularly on very thin skins.
8. The calf slunk can be made fairly transparent by thinning, humidity and pressure. The line of the infill can be made almost invisible by careful paring, glueing and controlled pressure from hand and folder. It is a matter of exploiting the working characteristics of the material. Some skins have naturally occuring areas of transparency or particular colour or texture that can be occasionally useful.
9. The lacing or sewing of a single leaf to its guard and the attachment of fragments or components to the 'parent' leaf is very sound practice. Our preference is to use calf slunk laces in widths and tones to suit the work. The pattern and spacing is largely dictated by the subject particularly if old perforations are to be utilized, say, from the previous oversewing. Infilling that is mainly cosmetic does not need sewing. The repair of healthy but physically damaged vellum can be entirely non-adhesive by using sewing and lacing methods only. Keep the proportions of the laces as fine as possible — the tensile strength of the lace need not be great, only sufficient to be used, pulled through the slots and tensioned lightly; a fine lace may lack strength

compared to thread but the accumulative strength of the stitches will be quite sufficient. The leading point of the lace is tapered and sized to stiffen it. When dealing with torn text or illumination lacing has been found functionally and visually better than overlays of transparent membrane. *(Figure 3.6).* If there is no room to place stitches in image areas then one can combine the membrane and lacing methods. Spaced groups of stitches or tackets will support quite long intervals of torn material without resort to overlays of vellum or membrane and the odd group can be worked in over image area if planned carefully — look for stepping stones.

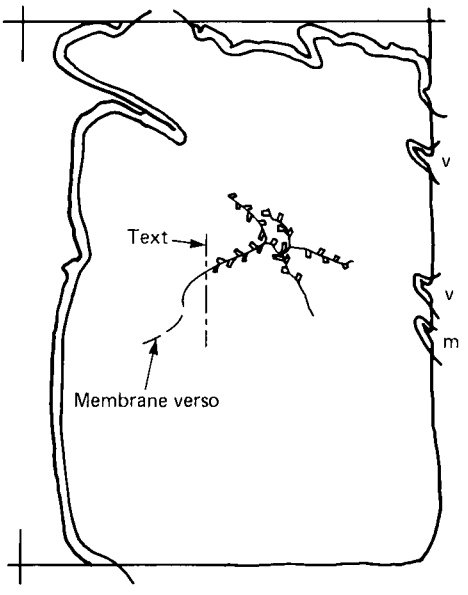

Figure 3.6. Drawing based on original control tracing for folio 94 of the *Book of Mulling,* TCD MS 60.

Sewing and binding

This aspect of the work will be discussed very briefly.

When sewing vellum manuscripts, follow the original sewing stations based on the evidence available — perforations, discolouration in the zones not overlaid by the sewing supports, impressions of the sewing thread in the spine fold. If the codex is to have a new binding, the earliest stations are used providing these give sufficient support. If not, supplementary supports could be added; for example, the original stations could be sewn double flexible and the supplementary stations utilize later perforations and be single flexible, or the latter configuration used entirely. Thick unbleached seaming twine is used and always pack sewn with reinforced kettle stitch. The spine folds are protected from the lining and covering adhesive by an insulation of paper in the form of a concertina (R. Powell) or single 'loose guards' (S. M. Cockerell). The boards of new bindings can be of quarter cut oak or laminated cotton furnish mounting board or the original boards. Endbands are sewn through the centre of every quire and, if necessary for support, the core laced into the boards. The covering materials we use are Harrold tanned goat[8], Italian or Irish goat vellum, Italian tawed goat and Hewitts tawed pig[9]..

Sample specifications

1. Eleventh-century Irish manuscript sewn double flexible on four 6/2½ cord linen netting twine and pack sewn through a zigzag concertina of hand-made paper. Vellum flyleaves and tawed goatskin joint glued and laced to the flyleaf. Endbands of seaming twine on a core of tawed goat. Boards of quarter cut oak cushion bevelled and rebated to take spine cover of tawed goat and joints. Pressure case of Burma teak (nineteenth-century) in the form of a slip case with the internal walls tapered sufficiently to give a light restraining pressure on the text block at 'bottom dead centre'.
2. Another for the 'average' manuscript — fifteenth-century Flemish. Sewn double flexible on linen cords through insulation of loose-guards. Vellum flyleaves with linen lawn reinforced handmade paper paste-down. Boards of museum mounting board composed of seven sheets of 2 ply cushioned and shaped. Laced-in endbands, linings of parchment and covered in full goatskin vellum not glued to the spine and with modern (German) tongued corners. Tight fitting heavy walled slip case lined with undressed linen and covered in linen buckram.

Exhibition cases

In the context of this paper we have mentioned the show-case and packing case systems that we designed to maintain a micro-climate inside the case that will conserve the equilibrium moisture content of the vellum. The show-case system was designed to reduce the daily handling of the early Irish manuscripts — Kells, Armagh, Dimma, Mulling, etc. Previously they had been exhibited in cases with no RH control or UV filters and had been opened and

closed each day and carried by hand to and from overnight security in the manuscript strongroom. In the new system the show-case carcase and its shatterproof and UV filtered glazing remains *in situ*. The manuscript is mounted on a linen-lined deck with secure but unobtrusive fixtures inside a polycarbonate glazed aluminium case or 'capsule'. The capsule containing the untouched manuscript is mechanically handled and transported to the strongroom. A trolley designed to hold five such capsules allows the operation to be done in one journey each way. The capsule is lifted to its station on the trolley mechanically. The system is comprised of five manuscript capsules and trolley plus one lifting unit and one trolley to transfer each capsule to its fixed show-case. Beneath the manuscript deck in the capsule is a cavity, vented to the deck above, containing several kilos of preconditioned silica gel (34% by weight) moisture buffer.

For the recent exhibition in the United States of the *Treasures of Early Irish Art* our manuscripts were transported from Ireland to New York and subsequently between venues in air conditioned packing cases. These cases were designed in collaboration with Nathan Stolow and supervised and participated in their construction and the packing of the manuscript. *(Figure 3.7)*.

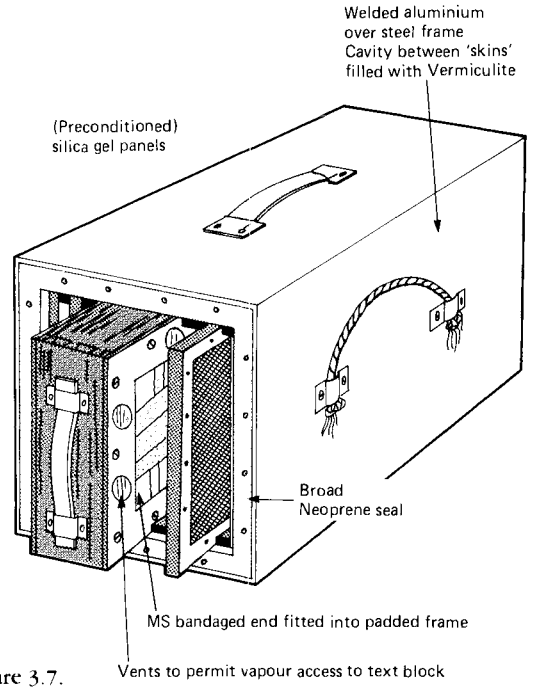

Figure 3.7.

The case is designed to protect the subject from impact and shock and to a large extent (fire door standard) from fire and water. The two panels of preconditioned silica gel maintain a stable microclimate. The materials used in the construction were inert and there were no adhesives other than casein (used for the mahogany support frames) and the soft tacky ethyl acrylate 'gum' on the padding sponge rubber.

There is no doubt that a specification could be worked out that would be cheaper; for example a marine ply carcase with a good thick lining of fire resistant thermal insulation with the manuscript packed in a shock absorbing material. The text block would be bandaged to reduce friction with cotton bags of preconditioned silica gel — all enclosed in a sealed plastic moisture barrier. One needs sufficient notice from the custodian so that one has time to do a good responsible job!

Equipment

Our stereoscopic microscope is the Olympus model X-TR (trinocular with provision for photography) with a working clearance of 90 mm and a magnification range of × 10 to × 80, and is usually mounted on a universal stand which allows the instrument to be poised over the work to a depth of about 320 mm. A good zoom binocular is also a very pleasant instrument to use.

The humidity cabinet

For a small cabinet of, say, 6 cubic feet a humidifier can be improvised by filling a small developing dish with a closely packed concertina of thick blotting paper inserted and adding water to about half the depth of the paper. *(Figure 3.8)*. We have used one of our washing sinks covered in a soft rubber edged sheet of perspex and find that an RH up to 95% at about 20°C can be obtained. The efficiency of this home-made evaporative humidifier is improved by placing a miniature fan close to the dish. The loss of humidity due to the opening of the cabinet is quickly recovered. With the evaporative system there is little danger of a precipitation of free water onto the manuscript, unless the cabinet is subject to a sudden drop in temperature. For this reason it is important to have good thermal insulation or a reasonably constant temperature maintained in the workroom. If one plans (as we do) to have a large cabinet, then the purchase of a commercially made evaporative type humidifier will be necessary (refer to Garry Thompson's *The Museum Environment*[10]). Models of the centrifugal type are not suitable for conditioning vellum. Small evaporative humidifiers are readily available.

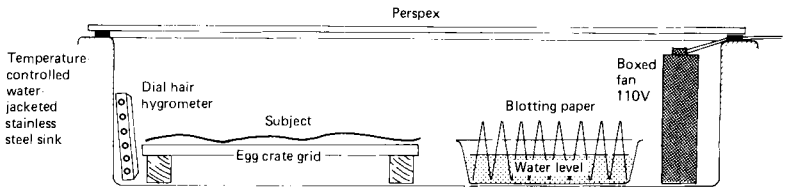

Figure 3.8.

With the increasing demand for preconditioned silica gel for the RH control of our manuscript show cases the need for a specially constructed unit has become more urgent. The use of preconditioned silica gel could be the basis for another totally safe, slow hydrating system.

Clips of the 'Bulldog' type (2½ in./64 mm) are used (with occasional use for the smaller sizes). The clips are dismantled and the jaw plates electroplated with cadmium (or if you want to be really fancy—nickel of copper) and then reassembled. The springs should not be plated as the electroplating process will draw the temper. The polished blue finish is fairly rust resistant. The jaws are lined with two rubber pads slightly larger than the area of the jaws 21 × 66 mm). We used Pirelli flooring rubber (mint green) 4 mm thick. The edges of the rubber blocks were rounded with a sanding stick and glued with Araldite epoxy resin. This thick packing of rubber ensures that the jaws are parallel and combined with a fold of blotting paper, avoids clip marks.

Needle awls made from ½ in. hardwood dowelling and number 15 binder's sewing needles. The dowel rod is cut into 2 ¾ in. lengths and shaped like a rifle cartridge. *(Figure 3.9).* This can be achieved by placing the dowel in a drill chuck and filing or in a lathe chuck and turning with a cutting tool or file. A flat should be left at the point to centre a 1.5 mm hole for the needle, which is held by a tight push fit.

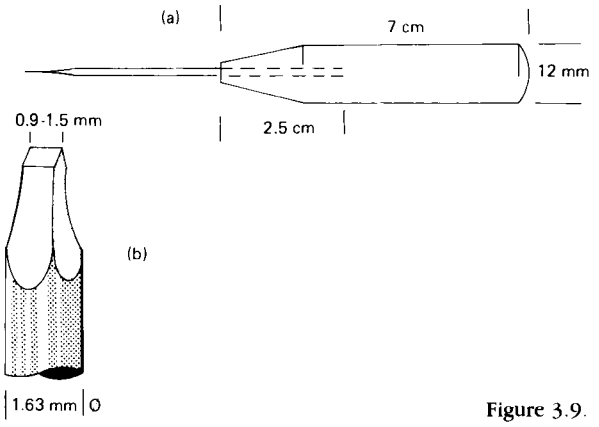

Figure 3.9.

Tensioning decks of soft insulating board (12 mm thick). Sheets are 8 × 4ft. so that subdivision of this can be made to suit the drying space available. Ours are cut to fit our trolley racks (61 × 80 cm) which means waste but the material is relatively cheap. This is large enough for most of our work. We have larger sheets sufficient to flatten full skins.

Pressing boards of plywood lined with matt white Formica.

Dental mechanic's flexible shaft drill and abrasive bits. The bits we use are by Meisinger, No. 658, which have a rounded cone shape. *(Figure 3.10).* This tool has proved invaluable for paring infills and guards of complex shape but is not used on the manuscript.

Figure 3.10.

Sanding sticks lined with fine grades of garnet paper by English Abrasives. Cut from dowel rod and narrow flat section beading. For neat results, pay attention to the machine direction of the paper.

Hardwood sander's block (beech or oak) — say, one foot of 3 × 1in. One side lined with contact rubber strip and the working face sanded smooth. *(Figure 3.11).* One side is broadly rounded, the other only very slightly so making is suitable for fine detail work.

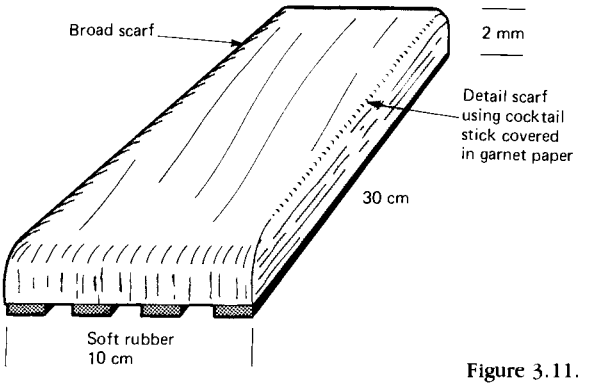

Figure 3.11.

Perspex offcuts in various sizes to protect the vellum from becoming too dry during repair work due to artificial lighting or during periods of low relative humidity in the workshop. If this becomes a serious problem then the room should either be humidified by some means or one must wait until

the ambient conditions improve. Ideally the work should be finally conditioned to the controlled RH of the strong room, say 55-60%.

Repair materials

Calf slunk:

The skins range between 2 and 5ft^2 and are obtained from as many sources as possible as each vellum maker produces a unique material. In the main our skins are prepared by Messrs Elzas and Zonen of Celbridge, County Kildare. We modify the basic material by scraping, pouncing and surface staining. See notes by Matthew Hatton of Trinity College Dublin in the Appendix below.

Goldbeater's skin, undressed:

We believe the transparent membrane we use to be the air bladder membrane of fish 'made from a tough form of connective tissue containing a fibre network based on a type of collagen which is called ichthuocoll' (Reed (1972), 131). We purchase our material from two sources:
Long and Long,
69 Roosevelt Avenue,
Belleville 07109,
New Jersey,
USA
and
Pierre Brenier,
31 rue Louis-Gaillet,
94250 Gentilly,
France.
who supply more crudely finished skins than Long and Long but which are equally useable and less. than half the price of the American product. Both products should be purchased for the same reasons as for purchasing a range of vellum. The Long and Long company call the material 'Transparent Natural "Goldbeater" Membrane'. They also produce other varieties, so it is important to use the above term when ordering. When ordering the French membrane we refer to it as *'feuilles de baudruche, transparents'*.

Edible leaf gelatine:

Each leaf weighs about 3 g and our working solution is 12 g/100 ml. Our material is made in West Germany for Rousselot Ltd, London and supplied through our local chemical supply company. We have samples of this material over twenty years old which are still bright, clear and flexible.

Acetic acid:

Add two drops of a 1% dilute solution to the gelatine (100 ml). Refer to Dr Reed's book. (Otto Wachter prefers to use wine vinegar and parchment size).

Sorbitol:

The humectant; we make a 20g/l solution and add three drops to the gelatine. One could call it a 'moisture conditioning agent'.

Heat-set tissue:

The receipe as used in TCD is given by Orla McMullen in 'Paper repairs in older printed books', *The Paper Conservator,* 3, 18—27 (1978).

Aniline staining:

Refer to notes by Matthew Hatton, Appendix below.

Paper:

Photographic blotting paper or water leaf without watermark.

Bondina polyester web, Type: 6050091:

Bondina Industrial Limited, Greetland, Halifax, Yorkshire, HX4 8NJ.

Appendix

Dyeing Vellum

The aniline dyes that we use are prepared by pouring one litre of boiling water onto one gram of the dyestuff. Stock solutions are prepared and mixed in varying proportions to achieve various colours. Tonal changes are effected with minimal amounts of dye. For example, if too much black is added to a brown, a green tinge will appear, due to the yellow in the brown and blue in the black.

For staining you must prepare the vellum by pouncing its hair side using fine garnet paper or pumice. Then relax the skin, using a damp pack of

blotters. This will help the dyestuff to penetrate the skin more evenly. To give a more even penetration, iso-propyl alcohol and ethyl alcohol were tried but resulted in the dyestuff coming out of solution.

When the skin is relaxed, submerge it in the dye bath and leave for a few minutes. When you feel that the skin has taken up sufficient colour, blot off the excess dye. You will notice that the flesh side because of its more receptive surface, has taken up more dye. This can now be modified by swabbing the surface evenly with a damp swab. Any unevenness in colour may also be adjusted. A second immersion may be used to darken the skin further. Clip and pin the skin and allow to dry.

It is advisable to keep a vial of the dyestuff from the bath for retouching the skin during repair, as the skin will be only surface dyed.

An additional technique if greyness is required, is to make a very dilute solution of the black and submerge the dyed skin for a few minutes. This will give a very fine film of black, imparting a greyness to the underlying colour.

Our basic preparation is:

(1) Bismack Brown RLS* (ICI) — 4 parts stock 1g/l.
(2) Baygenal Brown CGB (Bayer) — 100 parts stock 1g/l.
(3) Benzo leather fast black BH (Bayer) — 5 parts stock 1g/l.

The approximate amounts of the dyes used in the samples are:

(1) Baygenal Brown, stock solution diluted.
(2) Beygenal Brown : 1 litre + Bismack Brown 40 ml + Beygenal Black 60 ml.
(3) Baygenal Brown : 1 litre + Bismack Brown 40 ml.
(4) Baygenal Brown 1 litre + Bismack Brown 40 ml + Baygenal Black 50 ml.

*ICI sample dated 15/6/1943. The nomenclature may be obsolete but I do not know present equivalent. (AC.)

Matthew Hatton.

Notes and References

1. Reed, R., (1972). *Ancient Skins, Parchments and Leathers,* London and New York, 120.
2. Powell, R., Case history of repair and rebinding of an eighth-century vellum manuscript in Smith, P., (1974). *New Directions in Bookbinding,* London and New York, 173-174 & 177-182.
3. Belaya, I. K., (1969). 'Instructions for the softening of parchment manuscripts and bookbindings', *Restaurator,* 1, 49-51.
Belaya, I. K., (1969). 'Softening and restoration of parchment in manuscripts and bookbindings', *Restaurator,* 1, 20-48.
4. Methanol has been used by the writer for water-damaged vellum at the Biblioteca Nazionale Centrale, Florence. The technique used was immersion of the vellum leaf in methanol followed by insertion in a thin polythene envelope (to inhibit evaporation of the methanol and contact with this toxic solvent) and then manipulation to ease out the distortion.

Methanol is unpleasant to use, highly toxic and has no advantage over the ethanol/water solutions. The 'damp-pack' interleaving humidification is the most frequently used method in TCD (at the moment) because it lends itself to a balanced and efficient processing system of treatment for the normal run of distorted, but otherwise undamaged, vellum manuscripts. The moisture in the interleaving water leaf is controlled and checked with a moisture meter (Aqua-Boy). Contact between subject and the damp interleaving is prevented by an insulation of several layers of polyester web. The interleaving system requires careful preparation of the pack and very careful supervision; the process is rapid and requires precise timing.

Techniques and materials that change the original character of the subject, such as impregnation with synthetic polymers, humectants, plasticizers or lubricants are not used and are unnecessary if the storage or exhibition environment is stable and controlled (55-60%) and the equilibrium moisture content of the material maintained at the correct level to keep it flat and pliable. It is better to alter the environment than the subject. The TCD strongroom is maintained at 55-60% RH and our exhibition and packing case systems are kept at the same RH by the use of preconditioned silica-gel based on the recommendations of Dr Nathan Stolow.

The precise processing of the silica-gel requres a large humidity cabinet; our present improvised system for both vellum manuscript and silica-gel conditioning will be replaced by a unit designed to cope with the ever increasing demand for preconditioned silica-gel moisture buffer and the totally safe and effective humidification of vellum in quantity. The conditioning cabinet is

undoubtedly the safest device and the best way to humidify vellum manuscripts.

5. Stambolov, T., (1969). *Manufacture, Deterioration and Preservation of Leather,* ICOM, Central Research Laboratory for Objects of Art and Science, Amsterdam, p.55 (2.8, 2.2).
6. For methods of preparation and materials of the heat-set tissue used at Trinity College Dublin see McMullen, O., (1978). 'Paper repair in older printed books', *The Paper Conservator,* 3, 20.
7. The inlay is profiled and pared in a precise way with the aid of round sanding sticks, purpose-made paring knives and dental mechanic's flexible shaft drill and abrasive tipped tools which are of particular value, The Fortune paring machine fitted with a *very slow feed* worm gear can also be of value, providing the function of the machine is well understood by the operator — but used only for guards and large inlays — not the subject.
8. Harrold Manufacturing Company, Eagle Works, Harrold, Bedfordshire, England.
9. J. Hewitt & Sons Ltd., Tanners & Leather Dressers, Kinauld Leather Works, Currie, Edinburgh EH4 5RS, United Kingdom.
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3.1.2 The use of polyethylene glycol in the restoration of parchment

Vicente Viñas

The sensitivity of parchment and vellum to moisture and the dependence of these skins on moisture in order to maintain their physical and mechanical characteristics is well known. In fluctuations of moisture from one extreme to another, however, the skins are vulnerable to several alterations of a biological or chemical nature. The use of polyethylene glycol of low molecular weight for the treatment of parchment and vellum permits the maintenance of hygrometric constants and, therefore, the control of the physical, chemical and biological characteristics of these untanned skins.

The majority of the deterioration suffered by untanned skins is due to their hygroscopic characteristics. Because of this factor, in a dry environment, parchment loses water and becomes rigid like 'cardboard', cracks exfoliates, disintegrates, etc. On the other hand, in a very humid environment parchment absorbs moisture and becomes flaccid and weak, with a propensity for multiple chemical reactions by hydrolysis; it becomes an excellent culture medium for the proliferation of fungal and bacterial growth.

This hypersensitivity to water is due to the proper nature and structure of parchment. The flexibility and other properties that live skin possesses, such as skin tissue, are proportional to the equilibrium of its components and its ability to regenerate.

When an animal dies and is skinned, the skin begins a process of degradation that is controllable only by tanning which gives it, more or less, an insensitivity to water. However, untanned or partially tanned skins, as in the case of parchment and vellum, maintain their hygrometric condition despite the fact that in the processes used for their preparation a large part of their unstable components are eliminated from the actual dermis (epidermic layers, soluble proteins, sugars, glucose, fats, etc); this leaves a tissue formed by proteins that adopt a form of insoluble cementing elements; dermis and corium.

However, the insolubility of these proteins does not mean that they are indifferent to water. On the contrary, their elasticity is due precisely to water which acts like an authentic lubricant and a fundamental element for the configuration of the tissue (70% of animal skin is water which acts primarily as an intermolecular link, solvent, dispersant or vehicle of other substances; 3% is fat, primarily a source of reserve and energy). This is so to such an extent that characteristics are directly related to hygrometric state: it can disintegrate if dried, or be converted to gel in extreme cases of humidity and temperature.

As a result, the great capacity of these proteins for hydration and dehydration (in their double configuration as fibres and cementing elements) is due to the fact that parchment or skins which have not been tanned become sensible to hygrometric changes; this gives place to the alterations that characterize these materials. Actually, when they acquire humidity, the molecular links are increased due, particularly, to the hydrogen bridges. Their tissues reach greater flexibility until a point of dilution can be reached. The opposite situation

would cause rigidity of the skin, which in an extreme situation would cause brittleness.

In view of the above, the conservation of these types of skins is closely tied to variations of relative humidity in the environment. For example, the humidity absorbed in a few moments will be retained for days; in the meantime, the skin becomes vulnerable to alterations of a chemical or biological nature.

The theoretical answer to this problem is to maintain these materials in an environment of humidity and temperature that is in accord with their specific characteristics. But this poses difficulties in practice, because a strict climatic control would have to be maintained and the documents would have to be grouped according to similar physico-chemical behaviour.

However, these proteinaceous materials, because of their provenance, manufacturing procedures, types of inks and pigments used on them, etc. do not have a regularity that would permit mass treatment in a random manner. Thus, conservation treatment would be required on an individual basis.

Once this moment arrives, the solution would be to give each document of parchment or vellum the characteristics or properties that will permit hygrometric autocontrol. In this manner, one can dispense with a large part of the environmental conditions.

In order to achieve this independence the quickest solution would be to give these skins a tanning that would make them immune to climatic changes. This, of course, is tantamount to a modification of their original state and would cause possible alterations to the inks and pigments they carry.

The traditional treatment has been to 'dress' the skin with substances that are more or less oily and which, at the same time that they act as water repellants, 'lubricate' the fibres.

However, this system has certain disadvantages: application of the substance by rubbing in, a method that is slow and even dangerous for inks and pigments with the possibility of staining or causing transparent areas due to the impossibility of even distribution of the substance. The latter could, in time, oxidize and the feel of the document become oily with porosity decreasing, etc.

Because of the above factors, some years ago a search was initiated for a solution to the problem. It was concluded that control of the internal humidity of these skins was the most natural and suitable answer. However, this answer was virtually impossible to realize due to the physical unstability of water together with its chemical and biological problems. For this reason it was decided to use a substance that, although not water, would have the same positive effects. This substance was polyethylene glycol, of recognized application in other areas of conservation and in industry.

This water 'substitute', a divalent alcohol, is of a purely organic nature. Among its characteristics as applied to the problem it is non-volatile; it is virtually neutral pH; its viscosity can be regulated; it has excellent penetrability; it is stable to microbiological factors; it is a softener and a lubricant; it has an outstanding feature — its ability to regulate water due to its aptitude to act as a sponge; and, depending on the environmental humidity, it can absorb or reject water while maintaining its hygrometric constants. One drawback is that the product can dissolve some inks. Therefore, the appropriate tests must be made beforehand, and, if necessary, a fixative used before treatment.

In general, the technique used for some years by the Madrid Center is as follows:

(1) Fumigation, if required, followed by mechanical cleaning.
Procedures for fixing pigments. The pigments that are soluble in water, alcohol are (as indicated by a solubility test) fixed locally with a fine camel hair brush or with a fixing spray. *(NB:* the PEG does not affect mineral pigments or the classical agglutinates.) The fixatives generally used are Paraloid (B-72) dissolved in acetone or tetrachloroethylene; cellulose acetate film dissolved in acetone; an acrylic resin fixing spray (made by Pelikan Ag, Hannover, West Germany) dissolvable in tetrachloroethylene). Ensure that the pigments are not sensitive to the solvents contained in the fixatives.

(2) After cleaning the skin of surface dirt by mechnical means, if necessary, and fixing of pigments, if required, the skin is treated with water and alcohol, preferably by immersion. The proportions of the water and alcohol (ethanol) depend on the solubility of the inks and the porosity of the skin. Commonly about 30% water to 70% alcohol are used. The length of the time in the water/alcohol bath depends on the original condition of the skin. When the skin is supple to the touch it is ready for immersion. Thus the period of immersion can last from a very short time to several hours. In the meantime the skin is watched closely to ensure that the pigments remain fixed.

The purpose of the bath is threefold: (1) to clean the surface dirt that cannot be removed mechanically; (2) to swell the fibres of the

skin, soften them and facilitate the penetration of the polyethylene glycol; (3) to permit the elimination of folds, creases and wrinkles.

After the bath, the skin is pressed lightly between blotters for about 24 hours. During this time the blotters are changed a minimum of three times. The skin is then ready for the PEG bath. *(NB:* not all skins go into the PEG bath. Again, it depends on the condition of the skin. On many occasions the water/alcohol bath and pressing will suffice.)

(3) An immersion bath of polyethylene glycol (for synthesis — manufactured by E. Merck, Darmstadt, West Germany) with a molecular weight of 200 or 400. The PEG is used directly from the manufacturer's bottle — no dilution is necessary — at room temperature.

The parchment or vellum remains in the bath until the skin is transparent. No support material is necessary except in cases of fragile skins, when Reemay or similar material can be used. The skin becomes transparent when there is total impregnation, which can take days or even weeks, depending on the condition of the skin. Once this moment has been reached, the treatment is stopped and the excess polyethylene glycol is eliminated. This is done by placing the skin between a sandwich of porous material (e.g. Reemay) and blotting paper, then pressed using a roller and placed in a press under light pressure.

The blotters are changed several times as the polyethylene glycol drains off. The skin is left in the press until dry (three or four days). By this time the transparency will have disappeared. The skin will be flexible and will remain so, acquiring characteristics in harmony with its nature due to the hygroscopic stability of the product that has been incorporated.

(4) Lastly, the missing areas of the skin can be patched with stabilized parchment or vellum. The polyethylene glycol will not affect the use of synthetic or natural adhesives. Skins used for repair do not receive PEG treatment as the skins bought commercially for conservation are sufficiently stabilized.

Method of eliminating fixatives

If a sprayed-on fixative is used it is eliminated by an immersion bath. If the skin is fixed locally, the fixative is removed with the appropriate solvent using a cotton-tipped applicator.

3.1.3 A note on the structure of vellum and the effects of various solvents

Peter G. Ellement

Skin, the raw material of parchment and vellum manufacture, is an organ composed of several tissues the most important of which is connective tissue. This tissue is a complex system of cells and intercellular material which includes fibrous and non-fibrous protein matter. The most important of these proteins present is collagen which is a basic, hydrophilic protein. An explanation will be given of the chemical and physical properties of collagen and the changes which occur during the manufacture and ageing of vellums and parchments. This information will be used to suggest the mode of action of a variety of solvents applied to vellum.

This note very briefly outlines current knowledge of the chemistry and structure of collagen and discusses some of the ways in which softening agents are thought to interact with it. We will deal briefly with the structure of skin, and look at the molecular organization of collagen, because it is at this level that the interactions we are considering take place.

Vellum is traditionally produced from the skins of young animals. Skin is a complex organ, made up of a number of tissues, the most important of which is connective tissue, consisting of collagen, fat cells and elastin. All this is immersed in a complex inter-fibre matrix. During the production of vellum it is the removal of this inter-fibre matrix which is responsible for what the tanner calls 'opening up the fibre structure'. This enables chemical reagents to penetrate the skin.

If we look at collagen fibres in more detail we can see that a major fibre bundle (perhaps a millimetre in size) is made up of smaller fibres (perhaps 100 μ) which can themselves be divided into fibrils. Dividing these we get filaments (of about 20 nm in diameter) and even smaller protofibrils (about 5 nm in diameter). It is not until we get down to this level of organization that we begin to get cross-links occurring, the actual covalent bonds which bind the protein together.

The fundamental unit of collagen is the tropo-collagen molecule, a solid rod about 280 nm long, and 1.2 nm in diameter. The fibre structure is initially built up from the repeated joining together, end to end, and side by side of these molecules. The tropo-collagen molecule is made up of three chains of amino acids which weave around each other in a very complex way to form a triple helix. The stabilization that occurs in collagen begins here when bonds are introduced within this triple helix, and on ageing additional bonds are introduced between the heleses.

As we get older our skin becomes more wrinkled. It is gradually being tanned, by radiation and by chemical compounds in the bodies, and the wrinkles set into the structure. This happens when one makes leather, or when vellum is aged for a long time, is in contact with grease or is bombarded with radiation.

At a molecular level bonds are forming, producing a complex, cross-linked protein structure. These cross-links are covalent and will not be broken simply by the application of a chemical such as propan-2-ol. The fibre units have become fixed and one needs to bring about a breakdown of the bonds in order to relax the material completely.

However, in doing this, the protein is often damaged to such an extent that one never gets back to original material.

The inter-fibre matrix is a very complicated mixture of globular-proteins, which have come through the blood vessels in the skin and are surrounding the fibres. In addition, there are complex sugars which are bound on to the proteins (called proteo-glycans) and ordinary high molecular weight sugars called glycosoaminoglycans. This mixture holds the fibrils together, and is dispersed during the conventional alkaline process which is part of the production of vellum, creating the 'opening up' of the fibre structure.

This is necessary so that softening agents — fats in the case of leather — can penetrate between the fibres. Without it, it is impossible to attain the degree of flexibility required in bookbinding vellum.

Another characteristic of collagen is that it is labile to heat, that is, when heated it shrinks. The collagen fibre is also a hydrophilic unit. All along its length there are sites capable of binding water and various other reagents by hydrogen bonding. These sites are also available for taking part in covalent cross-linking with adelhydes and similar chemicals which may be present in the environment.

Materials like propan-2-ol and polyethylene glycols (PEGs) are suggested as softening agents. They do penetrate the skin structure and distribute themselves around the fibres, in this way allowing individual fibres to move over each other, which brings about a degree of flexibility.

In 1966 Kremen and Southwood[1] published the results of their investigation into the bonding properties of a range of poly-hydroxy materials, other than those of low molecular weight such as propan-2-ol, ethanol and methanol. They sorted out a list of materials, some of them similar to PEGs, which had excellent hydrogen bonding and penetration properties. As far as the author is aware, many of these materials, such as butyl carbitol and hexyl-cellusolve, are still untried as softening or relaxing agents.

Kremen and Southwood were very careful to balance the hydrogen bonding ability with the hygroscopic properties of the material because their work was aimed at finding a material which would bind on to hydrogen bonding groups in the skin, but which wouldn't rehydrate, remain sticky or produce problems with after-treatment of the pelt.

They found the best product for their purpose was di-butyl-carbitol, but there were a range of similar products which had very good hydrogen bonding ability, very good penetrating ability and were not lost from the structure quickly. Their work might well be worth looking at for anyone working in this field.

Reference

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3.2

Binding, Handling and Display

3.2.1 Preservation and display of single parchment leaves and fragments

Christopher Clarkson

A brief historical background is given to the dismemberment of manuscript volumes and the existence in collections of numerous single leaves and fragments. Some characteristics of parchment are described and emphasis is placed on how differently from paper it must be treated. The requirements of good matting design and technique are laid out and a description given of how they may best be met. A thread matting method — an entirely new concept — is introduced.

We wish to concentrate upon the problems surrounding the care and preservation of the small single membrane of parchment acting as a support for ink, paint and metal leaf decoration. We do not intend to discuss codices or large parchment sheets although some comments will be applicable to the latter and even more so to items conceived as a small single piece of parchment, such as deed, charter or indenture. Our subject divides into two types of item — a leaf from a dismembered manuscript volume or a 'fragment' cut from a leaf. Lack of margin, or the remains of one usually defines a 'fragment'. This may have been cut indiscriminately as with 'binders' fragments' or with certain discrimination as with cut-out miniatures or single letters.

The subject is not only of concern to conservators working in libraries and archives but also to those working in galleries and museums, because the most numerous group of single parchment fragments, and one which is always seemingly growing, appears to be those collections of items cut from medieval manuscripts in recent centuries, and forming part of 'study collections' in many museums and galleries.

Some idea as to how collections of such fragments came about is pertinent here because, first, their more recent history has probably complicated their preservation and, second, it may occasionally be thought more desirable to retain their later juxtaposition in, say, a collectors notebook or in a decorative composition than in presenting them as isolated fragments.

An entry in John Ruskin's diary of the year 1854 reads: 'Cut missal up in evening — hard work'.

In our profession we are fully aware that collectors, scholars and librarians have misused manuscripts throughout the centuries and this, of course, continues today, but such an entry comes as rather a shock from a man who could describe the almost mystical impact made on him by his first purchase of a small fourteenth-century Book of Hours: 'Truly a well-illuminated missal is a fairy cathedral full of painted windows, bound together to carry in one's pocket, with the music and blessing of all its prayers.' But at least his motives for such dismemberment were not simply for profit as is so often the case today; he would frame minatures and give them as gifts to little girls, or use them in a decorative scheme on a panel, such as that preserved at Bembridge, Isle of Wight. There was also an educational reason which we can best illustrate by quoting him: 'There are literally thousands of manuscripts in the libraries of England..... of which a few leaves, dispersed among parish schools, would do more to educate the

children of the poor than all the catechisms that ever tortured them'.

Ruskin seems to have lacked all liturgical knowledge and had little feeling for an illuminated manuscript as a whole. Personally, I find such dismemberment abhorrent, considering the retention of the historical intregrity of a volume essential, and as a conservator am concerned at the increased vulnerabilty to light damage and environmental changes of such separated items. But one finds that people in quite eminent positions often echo sentiments similar to Ruskin's, adding other arguments bearing upon their particular interest, such as ease of display, savings on insurance when loaning, and so on.

As early as the first half of the seventeenth-century Nicholas Ferrar's community at Little Gidding, Huntingdonshire, cut up volumes and prints with great diligence and with the spirited handling of knives, scissors, paste and a 'rolling press, rearranged fragments of text and illustrations to create the well-known 'harmonies' as an aid to religious instruction. [2]

Joseph Strutt, the engraver, produced in the last quarter of the eighteenth century books with many of their engravings copied from manuscript illumination, the source of each is specified and they brought this form of medieval art before educated readers for the first time. [3]

James Edwards, the son of William Edwards of Halifax who was credited as the inventor of 'those' bindings, was a bookseller who took full advantage of the unsettled state of Europe and imported whole libraries of books and manuscripts into England. Within twenty years he retired with a fortune, an estate and a magnificent library. At this period certainly a manuscript's size and weight was an element which could lead to its dismemberment. Linked to this factor was another which must also have led to vandalism –- on bound manuscripts and on books printed before 1801 there was an import duty of £6 10s. 0d. per hundredweight. [4] It would not have been surprising, therefore, for a dealer to jettison the binding and undecorated leaves before the reached the English Channel.

An important sale of such fragments, in this case initials, took place at Christie's on 26th May 1825, when there was dispersed 'a highly valuable and extremely curious collection of illuminated miniature painting ... taken from the Papal Chapel in the Vatican, during the French Revolution'. In this particular year, apart from the sale mentioned, Sotheby's held three others, totalling nearly 4000 lots. It is of interest to note that William Young Ottley, in his introduction to the Christie's catalogue, writes: '... those specimens (miniatures) are found in more perfect state of preservation than the frescoes and other large works of painting remaining to us of the same periods.' [5]

Amongst all the vandalism, one occasionally comes across a concerned voice. There is the instance of a sixteenth-century Flemish missal being hawked around the trade for a few years, in the course of which its original stamped binding was replaced, an act which aroused Dibdin to say 'Such a proceeding was little short of rank barbarism, and it is said the mister Charles Lewis, on receiving instructions to perform the operation, started backwards "three paces & mo — while "the lights" in his workshop burned blue'!! [6]

Such manuscript fragments were often stuck into albums, being grouped by subject and so forming study collections, yet others appear simply to have been formed by children as pastime recreation.

Not always are such cut-outs stuck into a blank leaf album or matted separately on card or panels. Add. MS.28784 in the British Library as an example where a complete late fifteenth-century Book of Hours has been embellished with full page miniatures from an earlier fifteenth-century Book of Hours and hundreds of pieces cut from a late thirteenth-century manuscript. [7] Such examples show the care taken in cutting and fitting — what was the intention or motive?

Such collections of fragments are of great concern to the conservator and unfortunately, as the thefts of miniatures from manuscripts at Cambridge or those at the Vatican in recent years sadly illustrate, are an ever-growing problem. Although stolen, one supposes through individual initiative, many such items find their way to study collections. In spite of the difficulties in formulating the ever changing attitudes of a past period, I do feel that it is worthwhile, over and above the standard condition report, to record points such as the measure of care with which the miniatures have been cut out. Nervous slashes around a miniature (cutting into neighbouring leaves in a manuscript) suggest a thief; but more careful cutting may suggest an owner desecrating his own collection. In building up provenance this is a point as important to record as types of adhesive, backings, fragments of marginalia or library stamps.

I am not sure how much the differences between paper and parchment should be laboured here. Many conservators are as despairing as I at the number of parchment items mistakenly given aqueous treatments, placed in dry mounting presses or laminated. I could show photographs of the deformed and shrivelled remains sent to me. Perhaps the despoilers will never make the same mistake again, but with so many people coming into

the field or library and archive conservation, can we afford such mistakes?[8]. I am not going to stress such differences here, except those that apply to the problem of matting single parchment pieces.

The main feature in parchment (vellum) making is in drying the wet pelt whilst it is under tension. This simultaneous action of stretching and drying brings about peculiar changes quite different from those applying when making leather. Reed has expressed this well 'These are (1) re-organization of the dermal fibre network by stretching and (2) permanently setting this new and highly stretched form of fibre network by drying the pelt fluid to a hard, glue-like consistency. In other words, the pelt fibres are fixed in a stretched condition so that they cannot revert to their original relaxed state: the result is a product which is a taut, highly stressed sheet, relatively inelastic and having a stiff handle.'[9] A vertical section of parchment placed under the microscope will show an almost zero angle of weave.

Parchment is an extremely hygroscopic material and will readily respond in area and thickness to changes in the surrounding relative humidity. In fact strips or parchment are sometimes used as the responsive element in hygrometers. Paper, cards and woods move less and at different rates. An important point is that parchment, being of biological origin, absorbs and gives up moisture in a varying manner over its whole surface — therefore the degree of relaxation or shrinkage is variable also — and each skin will react differently according to the animal type, its diet, its age and, possibly above all, its processing, creating a highly individual material which tends to outwit any grouping or standardization of technique.

If parchment is allowed to absorb a great deal of water, then the stressed fibre network held in the ground substance will relax and during uncontrolled drying reorientation of the fibres in that area will take place causing loss of flexibility, loss of opacity and shrinkage resulting in distortion of the surrounding skin.

The way to learn about a particular parchment's reaction in varying environments is to try and frame it and watch it through the seasons of at least one year. Parchment *en masse*, as in a closed text-block, is slower to react to environmental fluctuations than are the displayed leaves of an open volume or the mounted single leaf or fragment. A single membrane of collagen suspended within a mat is immediately sensitive to variations in moisture content and will change dimensionally. A strip of parchment 14in. long by 1in. can alter in length 3/16in. in a 15% change in relative humidity. With such dimensional changes any decorative layer[10] will be affected. Parchment, being a natural material, will vary in consistency and degree of movement, not only between different areas of the skin, but between the same areas of different skins.

In matting single parchment leaves there appear to be four schools of thought:

(1) — Ignoring its life and spirit altogether by humidifying it and then sticking it down overall to a card, paper or wood support, struggling with it and pressing it till it stays down, subjected, beaten and defeated, or so one may think. The problem is that unless destroyed it will never give up the struggle (unless it is so weakened that it splits in two) and tends to outwit and, of course, outlive one.

(2) — Treating the membrane in a similar way but only drumming down (sticking around the edges). In this method the adhesive line usually breaks down along two edges, thus allowing dramatic diagonal distortion to occur across the item. Where the adhesive bond is too strong the parchment will split across from its weakest area and then be free to distort.

(3) — Treating it as though it were paper, guarding it or hanging it from its head edge. But it is not a cellulosic material, and however carefully the local environment is controlled, it will move and distort.

(4) — Accepting the 'life' of the parchment and simply sandwiching it between glass or acrylic sheet: a method rather insensitive to the character of the material and, of course, stopping any study of the physical nature of the item. In certain cases where the item is particularly weak, it can be argued that such methods are the only safe ones for storage and display. Damage can occur to the item, particularly if environmental recommendations are not strictly adhered to. I am also alarmed by the number of acrylic sheets seen over friable paint layers; the static pull is considerable, especially at grand exhibitions when energetic cleaning firms polish each case and frame nightly.

Unsympathetic matting techniques will cause distortions as the items are studied, transported and exhibited. In considering the long-term care of such skin items, the matting technique should become an integral part of the preservation requirements and therefore must be considered as such. Such a preservation matting design should fulfil the following requirements if it is not going to be pulled to pieces by the user attempting to view covered areas or be physically damaged in other ways:

(1) Such parchment fragments should display their very edges, particularly if they are fragments cut from a manuscript volume.
(2) It should always be possible to observe the reverse side of the item without having to touch it, even if this appears to be blank, the skin used and its preparation being part and parcel of an item's study.
(3) Protective boards are preferred over any kind of transparent covering film or tissue. If there is a case for having transparent film covering a particular item, only Mylar or Melinex will be used, and the film should be of such weight and so attached to its spacing frame that it will be taut with no risk of sagging over a period of time.
(4) If protective boards are hinged to such a mat, these should be able to hinge right back in such a way as to allow either face of the item to be exhibited.
(5) The preservation matting should be of a type which will allow a mat-surround of different colour or texture to be superimposed over it, according to the dictates of the exhibition.
(6) Instructions to prevent re-matting of item for each exhibition are essential. Such a requirement includes standardization of mats and frames.
(7) Storage boxes should be tailored to fit standard dimensions of the mats, so no mat will slide around in its box. The box should be of a design that allows a mat to be easily removed or replaced with two hands.
(8) All mats to be made of finest all-rag archival quality board.

Concerning the manner and technique of matting, I set myself the following aims:

(1) Preserve in every way possible the individual quality of the skin and its surface treatment.
(2) To attempt to understand and work with the material.
(3) A form of mounting should be chosen which will support the skin all round, not over-stressing it, yet readily 'giving' to expansion or contraction if by accident the chosen atmosphere alters.
(4) The method of support must include a breaking point judged to be weaker than the weakest area of the particular membrane.
(5) When framed, a generous distance should exist between parchment and glass (for instance, at least ½ in. for a sheet 20 × 16in.).

The main difficulty is to find a method of supporting the parchment, as it were, in mid-air to support it around its entire edge so that one has control over all surface movement. A method of support is required which would expand or lengthen when the relative humidity drops and the parchment sheet contracts, and will contract when the relative humidity rises and the parchment expands. This excludes paper, parchment, loosely spun yarns, synthetics, etc. I experimented with various elastics and soft springs but such methods tend to be of uncontrolled contraction and expansion.

Other considerations, such as that of the life expectancy of such support material, limit the range of choice, as does complexity of construction; simplicity being a great asset for future maintenance. One does not want a method which, as parchment contracts, will increase its tension. What one requires is a material which will contract or shorten in a *measured* way when the parchment expands, and expand or lengthen in a *measured* way when the parchment contracts.

At this point I wish to clarify an important factor; one which too often is not considered. We understand that a parchment sheet must be able to move, to 'breathe' within a frame; but because many parchment leaves are merely acting as a support, such a statement is too simplistic. The tolerance that one can allow on such movement of the parchment sheet must be directly related to the particular characteristics of the decorative layers of an item. For example, where such layers are all thin washes or merely tints left behind in areas of paint loss, considerable movement may be tolerated. But where at least one of the decorative areas is thick, then such movement must be closely controlled. Other factors which must always be considered in association with this are the dimensions of the sheet and the dimensions of the vulnerable decorative layers. For example, the large areas of gold leaf in a thirteenth-century Italian miniature are more susceptible to crazing and flaking than the small areas of gold dotted over the surface of a fifteenth-century French miniature.

The best material which I have so far found to form such a controlled support material is 'hard' spun thread, for when the fibres of such a thread expand the twist increases and the total length of thread shortens. Echoing one of the indelible rules of our camping days — slacken guys when it rains, tighten them when the sun comes out. The definition of 'thread' from the Oxford English Dictionary is 'A fine cord composed of the fibres or filaments of flax, cotton, wool, silk etc., spun to a considerable length, such a cord composed of two or more yards twisted together.' The critical characteristics to

consider for our purpose are the hygroscopic features of the fibre used, the angle of twist and the compactness of the twists. The greatest 'hardness' (the greatest twist) depends upon the nature of the fibre; of course, if twisted to an extreme, the thread will kink and curl, a feature not required. Several threads may be laid together and spun again to give a ply or 'double yarn'. Commonly the direction of twist of a ply will be opposite to that of the thread used; thus if the threads are 'S' spun, the ply will be 'Z' spun. In my present methods of matting, a small portion of each supporting thread shows around the edge of the item. 'Plys' would look rather clumsy and so to date I have not experimented with them.

Thread or paper strips attached to the corners of a sheet of paper or parchment have long been used when constraining the item between a sandwich of glass or acrylic sheets. What is described here is in no way similar; for if one supported unsandwiched parchment only at the corners, it would be free to allow some areas to relax or contract in an uncontrolled manner, so over-stressing other areas and causing distortions and damage. Success depends upon attempting to distribute expansion and contraction evenly over the entire sheet. One will thereby cause minimum movement of support to occur under any particular decorative area. An ideal support for this single stretched membrane would be to attach it in a continuous manner to a sympathetically expansive or contractive sheet material. Unfortunately, I have across no such material with which to experiment. Before acceptance of any item with heavy decorative layers, I obtain environmental records from their present storage and set the workshop atmosphere similarly. I stress to the client the difficulty in matting and framing such items. Only if they feel happy that they can maintain a stable atmosphere at the item's final resting place, that is with only about 15% variation, will I proceed. I usually suggest a thread-mounting method be used with breaking points at one or other end of the thread, to prevent distortions after matting. The parchment item must be worked and matted in similar atmospheric conditions as those in which it will be stored and exhibited.

Although this particular paper is not the forum in which to discuss conservation techniques, I would like to stress that I am alarmed that, because of the void which exists between painting conservation and that of library archive materials, much of real artistic merit has been, and is being, lost.[11] To give just two examples:

(1) The prepared surface or 'velvet' of the parchment subtly varies, indicating production, period and locale. Such clues are easily lost through crude methods of humidification and pressing.

(2) The delicate refractive modelling with glair of flat areas of colour is being lost by crude applications of consolidants. Much of the blame for such damage rests heavily on the major libraries, who for far too long have encouraged mass and semi-mass treatments to be carried out upon unique items, often of high artistic merit. We argue strongly for satisfactory storage, handling and display environments[12] and less for a ready use of synthetic impregnations. A good humidity chamber is essential, one which is capable of very gradual and controlled humidification, particularly when the parchment has heavy decorative layers. I tend to work as dry as possible, using water sparingly, when needed, and adding ethanol or isopropanol if required.

It is certainly not a foregone conclusion that future preservation of such a parchment item is best served by removal of its backing. Such work has many risks and that of loss may be judged too high for my present techniques. I certainly feel this about B.L. Add. MS. 18851, mentioned earlier. Another factor is that it may be judged that a particular item has reached an equilibrium with its backing and should not come to much further harm if left.

The successful matting of a parchment item depends to a certain extent upon it being a well-balanced item. The contracting influence of layers of unremoved adhesive, particularly those of animal glue which nineteenth-century collectors and booksellers appear (surprisingly) to have used so freely, must be removed, or at least patiently thinned till its membrane effect is broken as far as possible or it will give endless trouble in later years. The aim must be to achieve a balanced parchment sheet which a varying atmosphere will influence equally from either surface.

Basic technique of simple thread matting

The item is ready for matting; it has been lying under a lightweight board in a stable workshop atmosphere 2—3% RH higher than its final resting place. Choose a hand-spun pure linen thread; its atmospheric response will be more reliable if the dressing is removed by washing it with a little soap. Do not lose any twist; make up into a skein and leave taut between two soft springs until dry. Next, one must determine the length of one of the two pieces

of thread required. This will depend on two basic factors, the surface area of the item and the degree of mobility inherent in the skin. For example, two pieces identical in size may move quite differently. Equally, a small fragment from the belly area of the animal may need threads longer than a large piece from the butt, because of the different mobility rates determined by the degree of compactness of the fibre bundles. However, at present I have no way of measuring this variable accurately[13] so in practice the length of each thread is partially determined by judgement regarding the mobility of the parchment. The other factor which must be taken into account is the type of thread to be used and the amount of twist given, as mentioned above.

The reader may wish, of course, to carry out personal experiments, but as a rough guide, for a parchment fragment cut from a manuscript leaf and measuring 8 × 6in., we would probably supply a free movement of linen thread ranging somewhere between 3½ and 4½ in. Once the length of free movement of thread is determined, we add another inch for the anchorage points. Cut the threads to equal lengths, and as many in number as to go completely around the edge of the item at ½-¾ in. intervals. The space between the threads is determined by the same factors concerning choice of length of thread, as well as the presence of any text or decoration (of course, one must avoid as far as possible attaching thread to any surface markings). The distance between lines of text often determines the spacing of the threads. Always one must be conscious of supporting the edge of a piece of parchment: if the space between threads is too much, then the parchment membrane will gradually distort, developing shallow 'engrailed' edges.

With a needle, tease one end of each thread into a small fan shape. With the parchment lying verso up and all but one edge covered by a lined board of light weight, attach the threads by their fans in such a way that they radiate out at angles judged to supply the maximum support to the item *(Figure 3.12)*.

I often use paste for this purpose because of the fact that, not having an affinity with parchment, it will create a simple direct 'break point', the paste's particular dilution being a controlling factor. With the threads attached all around the parchment, the next step is to cut and prepare the mat.

The format of the item, along with its flexibility, will determine the thickness of matting card required; this will be at least four-ply to give protection for heavy decorative layers and/or slight distortions of parchment. The format size must allow for wide margins which cover the full length of threads radiating out from the item. If the verso of

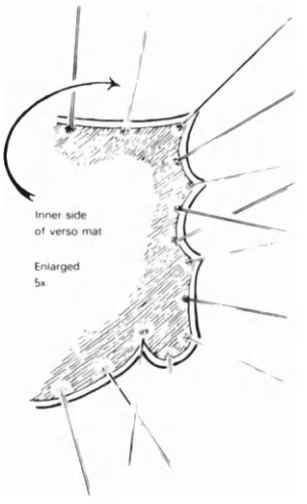


Figure 3.12.

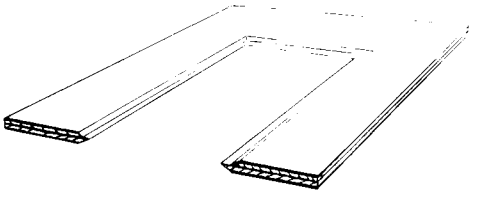


Figure 3.13.

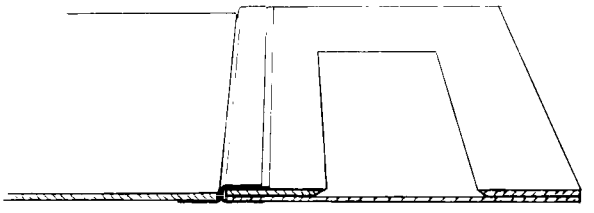


Figure 3.14.

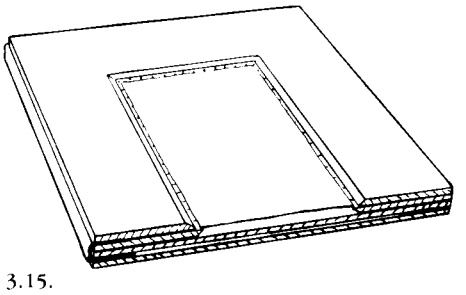


Figure 3.15.

item allows, then one can cut the mat window so that the bevelled margin overlaps the edge thus supplying support *(Figure 3.13)*. If this is not desirable, then both windows are cut, with a bevel, to similar shape and size being an exact silhouette of the item with an increase in area of ⅛ — ¼ in. all round. One requires the card as close to parchment edge as possible for reasons of support, but not so

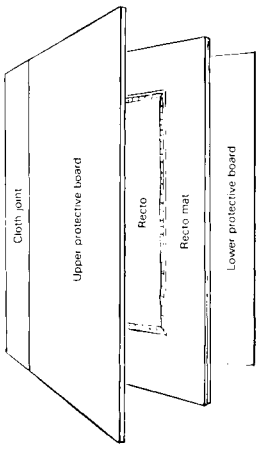


Figure 3.16.

close as to hap and buckle it if the item expands. This is the reason my mats are silhouetted, which occasionally may look fussy and detract from the item. This latter can be counteracted at exhibitions by overlaying with a map having an oblong cut window.

The protective board wings are hinged with good quality linen book cloth to the inner side of the verso, or base mat *(Figure 3.14)*. The joints must be wide enough (two cards plus two cloths) to allow protective boards to fold right around and lie flat to expose either face or item for framing *(Figure 3.15)*. When all is dry, the mat is laid out with offcut from verso window temporarily replaced and upper protective board thrown open. The item is carefully centered and threads radiated. Starting in symmetrical order from corners, or from centres of edges, according to the particular problems, one proceeds to glue ¾in. of the end of each thread in place, carefully obtaining the best supporting 'angle-to-edge'. I use a stiff PVA emulsion for this and each thread is spun, as it is attached, to increase its twist. It is important that the rest of the thread is left free to expand and contract. When all is completely dry the recto mat is set in place over the threads. This is held by placing a few small spots of adhesive between threads, which allows for easy removal of recto mat for purposes of future maintenance. The protective boards *Figure 3.16)* can carry a written record of the RH in which items were matted, and instructions to user and exhibitor, index number of conservation report or any other relevant information or warnings.

Notes and References

1. Cook and Wedderburn (eds.) (1908). *Praetorita iii, Works of John Ruskin,* XXXV, 490-491.
2. A contemporary description '...each passage was fitted to the next belonging to it, with nice knives & scissors, & afterwards pasted onto the best & strongest white paper, so evenly and smoothly, by the help of the rolling-press, that many curious persons who saw the work when finished were deceived, & thought that it had been printed in the ordinary way'. Acland-Troyte J. E., (1888). 'An account of the harmonies contrived by Nicholas Ferrar at Little Gidding', *Archaeologica,* 51, 189-204.
3. Bodley MS, Douce e. 18 entitled 'Mr Strutt's account of the manuscripts that have illuminations, as they occur in various English libraries (with corrections) and additions by F. D.', E. R. Mores had produced a small series of engravings copied from miniatures in 1754 (see Carter, H. and Ricks C., (1961). *Edward Rowe Mores'*. Oxford xxi-xxiv). Richard Rawlinson (1690-1755) had also done similar work. His original copper plates passed with his collection to the Bodleian Library. But such facsimiles produced by both these men were small editions and for special purposes.
4. *Phillips Studies,* (1954). iii, 33-35.
5. *Catalogue,* Christie, 26 May 1825, 3.
6. British Library. Add MS. 1885, 1
7. Oliver, J., (1979). 'Reconstruction of a Liege Psalter — Hours', *British Library Journal,* Fall, 107-128. Miss Oliver states' ... such mutilations appear to rest with the 18th or 19th century owners'.
8. Just one example for those who think the author exaggerates: please read: 'How do you mount an old wrinkled sheepskin?' by Jim Armstrong in *Framing and Fine Art,* (April/May 1977). 55-59. How does such an article get accepted in a magazine which has some noted conservators on their reviewing board?
9. Reed, R., (1972). *Ancient Skins, Parchments and Leathers,* London and New York, 120.
10. 'Decorative layers', in this paper, also refers to areas of text.
11. The disregard for manuscripts which this paper illustrates continues to the present day. It shows up in such things as the poor housing, servicing and security of many libraries compared with museums and galleries; by lack of interest of the conservation world in general and by custodians who have not understood the material needs of such items on their shelves.
12. In too dry an atmosphere a parchment skin will give up too much moisture, becoming dry and tending towards brittleness. Such em-

brittlement has been ascribed to the loss of waxes and oils from the skin, and various treatments have been suggested to remedy the situation. We are sure that in the majority of cases loss of water is largely responsible and not loss of oils and waxes. Placing various types of processed parchment in extremely dry conditions will demonstrate how quickly the most flexible of skins can be turned into a hard, distorted structure. If they are then placed into an atmosphere of higher humidity, flexibility will rapidly be restored. Changes in the natural wax/oil content of the samples do not appear to occur under such circumstances. Correct and stable storage conditions are vital.

13. Overnight during the Cambridge 1980 conference Sydney Cockerell devised a measuring instrument similar to a hygrometer, which consisted of a pointer attached to a good-quality bearing, moving across the face of a dial. Samples of materials whose relative expansion/contraction were to be measured could be easily changed. In experiments to demonstrate the working principles and method, Cockerell took a parchment strip which he then lightly sprayed with water. The pointer registered a clear expansion. Then he exchanged the parchment for a length of hard-spun linen thread and sprayed this. The pointer clearly registered a contraction. As far as we know, no-one has yet experimented with standard-sized samples of skin, both from different areas of the same animal and from the same area of differently processed skins.

Discussion Notes

Preparing site of attachment for threads

In response to a request for further information on this matter, Clarkson explained that a small amount of paste is put onto the parchment, avoiding any pigment areas, and the parchment is not scraped up in any way to prepare it for the paste. The fanned-out end of the thread is then placed onto the pasted area and pressed out with a bone folder, trying to keep the fan as small as possible. The adhesive will withstand moderate sidepull, which is all that is necessary, and will peel off readily. One manuscript leaf, sent from the National Gallery in Washington to West Germany, did break away from the threads, when subjected to an estimated 15% RH change in the aircraft taking it over. The parchment was not damaged, demonstrating that the anchorage point therefore also serves as a breaking point. Vellum drummed down on a stiff board has no such breaking point and may, for example, tear across an area already weakened by mould because there are no weaker breaking points. Although this is an elaborate method of mounting single leaf fragments, it appears to work well and there appear to be no viable alternatives.

Is it possible to show both sides of the fragment right to the edges of the fragment?

Provided you can walk round the item, this is possible. In the National Gallery Exhibition, the exhibits were placed in pedestal stands designed by John Krill with a flow of air from floor to ceiling, and an inch space on either side of the parchment sheets. One dummy wall had cut outs in which showed the recto on one side and the verso on the other, but it had a good air flow and there was no movement. This is important, as a large crowd in a congested exhibition room will create problems with the relative humidity.

Upper and lower limits in changes of relative humidity

This is an important point. Environmental engineers reported before the workmen started on the above mentioned exhibition. A 10% tolerance either way was allowed in the RH level, which is the range the mounting system can cope with. Experiments have shown that a 15% change can be tolerated, but that sort of fluctuation is too much for some miniatures, especially the thirteenth-century ones with heavy sheets of gold. The engineers were able to provide the conditions required. It is essential to work within these strict tolerances.

Maximum size of vellum leaf suited to this technique

The largest handled so far was the size of the large twelfth-century folios, almost the whole small goatskin size 2 × 3ft., and this worked well. It is very important to have wing boards, or protection boards, of sound material so that they support the material as you move it round. It is very important to equalize the air flow on the verso and recto of the

sheet, as the side exhibited tends to get a greater flow of air across it. The frame must be dsigned to equalize the flow. It is basically a system designed for small pieces.

Removal of manuscript fragments from early bindings

The question was raised by Judith Segal of the Bodleian Library about requests from readers to lift pastedowns made from fragments of manuscripts so that both sides could be seen. Dag-Ernst Petersen explained the policy at Wolfenbüttel, which to some extent depended on the condition of the book in question. If it was in perfect, original condition, then the request would be refused. If the pastedown was already partly detached or had been lifted and pasted down again, then it was likely that permission would be given. However, in all cases the librarian first asked the conservator whether the fragment should be lifted. Christopher Clarkson added that the wholesale removal of such fragments, which were seldom referred to subsequently, was a disgrace. Only by being left *in situ* do such fragments give information about the technique, country and period of a binding. Their removal should only be allowed if the case for their removal can be proved beyond doubt, and then it is vitally inportant that the details of how and where the fragment was used in a binding are recorded and kept with it.

Flaking and loss of heavy layers of pigment and gold leaf

A general request for information about research in this area by Lilly Hollander was first answered by Dag-Ernst Petersen, who reported that the week-long conference at the University Library in Bremen in 1979 failed to come up with any definite answers. The use of parchment size on the surface of painted areas was objected to because it tended to alter the refractive index of the colours and so change their appearance. Christopher Clarkson added that the use of soluble nylon on the surface of painted areas would have the same effect, but added that where the paint layer or gold was flaking, rather than friable, it was possible to get under the layer and bind it back onto the support material. Where it was friable, there were bound to be problems with altering the refractive index, and a lot more work needed to be done urgently to prevent the continuing loss of fragments. Asked by Tony Cains whether rehydration could not help bind the pigment back to the vellum, Petersen replied that the moisture could reactivate the binder used in the pigment and re-attach it. Clarkson expressed doubts as to whether this would be enough to re-attach a flake that had come away cleanly from the vellum.

3.2.2 Notes on the binding and storage of vellum-leaved books

Dag-Ernst Petersen

This brief paper is intended to demonstrate parchment both as a writing and a binding material, taking examples from the past and the present. As a restorer at a library (The Duke August Library, Wolfenbüttel, West Germany) which is rich in older holdings, the great extent to which parchment has been used in a variety of ways in the general make-up of bookbindings has become clear to the author. Indeed, towards the end of the Middle Ages limp bindings are found which consist exclusively of parchment. The overall uses of this material and examples demonstrate to what degree parchment or vellum has — or has not — proved itself as a binding material, as such knowledge can be of valuable assistance to the restorer and conservator. The durability of parchment was known early to bookbinders, but its use did not correspond in every case to specific needs. It seems always to have been considered a relatively expensive material, as evidenced by the many manuscripts which were cut up for re-use for other purposes or even were written on again. Today an aversion to parchment is felt by many restorers and bookbinders. Admittedly its preparation is not always easy, and it does react quite differently to paper and leather. The following is intended to be an encouragement to all those involved in these fields to put more trust in vellum and parchment.

A short historical survey may be useful in throwing some light on the importance of this expensive and durable material through the centuries. The following list illustrates the major possibilities of the use of parchment in bookbinding in the past and today.

Parchment as a writing material

Parchment is probably the most durable organic material of all, many manuscripts hundreds of years old surviving in which the writing support is still in perfect condition. Its strength, folding endurance and flexibility are maintained to a remarkable extent, given the correct climatic conditions for its storage (a certain amount of atmospheric humidity, allowing the skin to absorb moisture from the surrounding air, is essential for its flexibility).

Folds for strengthening the centres of gatherings

A parchment fold placed at the middle of gatherings is frequently encountered in medieval paper manuscripts *(Figure 3.17)*. This protects the leaves when they are sewn together and stops them from tearing. Moreover, it increases the swelling of the book, which is mostly very desirable when thick handmade paper forms the textblock. (Of further passing interest is the fact that such strips may have been cut from earlier manuscripts and can on occasion allow the reconstruction of valuable texts.)

Figure 3.17.

Endpapers, pastedowns, fly leaves

Parchment endpapers can fulfill their task of protecting a book's outer leaves effectively and long-lastingly *(Figure 3.18)*. They were used both in conjunction with wooden boards and with pasteboards. Parchment used as a pastedown can help to keep a board in its right shape, i.e. slightly convex.

Parchment/vellum as a substitute for thread

In limp vellum and related bindings one can see narrow parchment strips used in place of thread as a sewing material *(Figure 3.20)*. The durability of parchment used in this way is enormous.

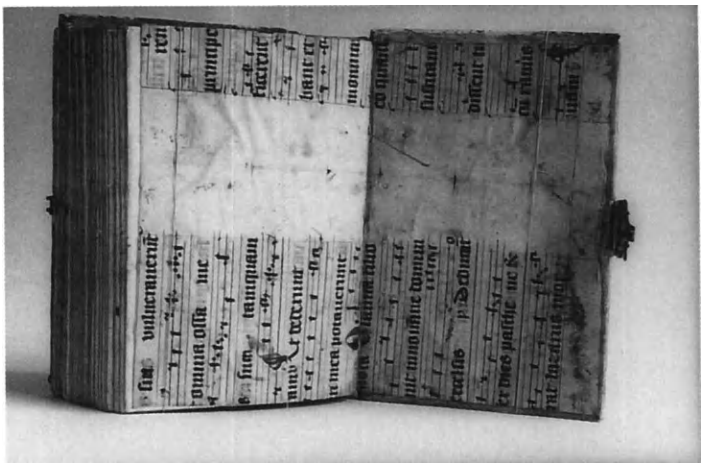


Figure 3.18.

Inner joints

In books with wooden boards parchment often provides the material connection between the bookblock and its cover *(Figure 3.19)*. In a number of such cases one can observe that the mistake was often made of adhering the parchment too rigidly, which resulted in it tearing away with the first gathering of the book or in the splitting of the joint. The demands made on the structure by pulling and folding when the boards are open and closed are very great. These days, the parchment joint is usually pasted in when the board is wide open, thereby avoiding too great a strain.

Sewing support

From the sixteen to the eighteenth centuries stiff-board vellum bindings were frequently sewn on parchment strips or bands. These strips, about 10 mm wide, placed singly or doubly on top of each other, were split where they projected over the joints and the narrower portion was laced through the vellum cover. Subsequently both halves were pasted side by side to the inside of the board. It is now known that in most cases such structures did not last. Either the parchment of the cover has torn along the joint or the strips have broken through the movement of the boards. Even if the sewing

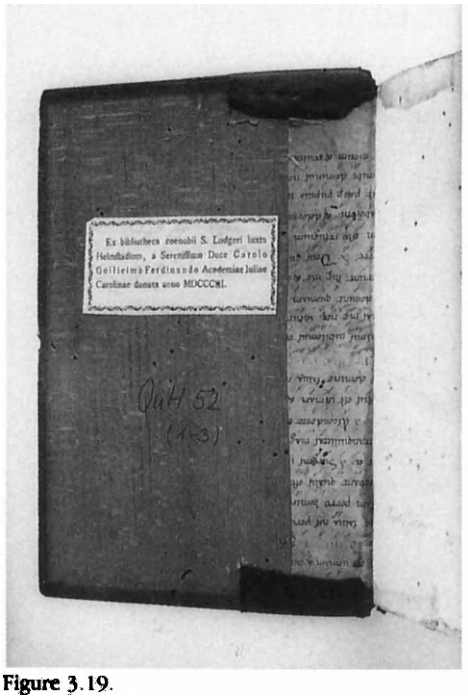


Figure 3.19.

Figure 3.20.

support in the spine has survived, the demands made on the joint have proved too great.

Spine lining

The wisdom of lining the spine of a book with parchment is disputed among restorers. Libraries provide examples where the spine lining has been responsible for totally deforming the book itself. The reason for this is that in conditions of fluctuating humidities parchment can develop strong pulling power, whereby the original rounding of the spine is drawn into a concave shape. On the other hand, books with parchment spine linings may be precisely those which strike the eye with their faultlessly well-preserved shape *(Figure 3.21).*

Such differences derive from the differing procedures followed in using the parchment. In the former instances the parchment lining strips on the spine are positioned between the bands with their ends pasted to the inside of the boards. In the latter it is a question of two lining strips lying across each other on the spine, both of whose ends are pasted to the boards. We have observed a very good and durable way of spine lining in France. From a strip of parchment, measuring about one and a half times the width of the spine and the height of the bookblock itself, pieces are cut out to match the size and position of the bands on which the books are sewn, so that the spine is pasted down with parchment between the bands. The projecting portion of the spine liner, the full length of the spine, is then pasted onto the adjacent board as the inner joint. Since two of these strips are applied

Figure 3.21.

along the spine, each with a projection onto a different board, the parchment over the spine is of double thickness. This is probably why a book with such a lining keeps its shape for a long time. This technique was much used in books both with hollow or tight backs bound in Paris in the seventeenth and eighteenth centuries. Glue and paste were used as adhesives.

Endband cores

Narrow parchment strips, laid several times across each other *(Figure 3.22)* or rolled together, were often used as endband cores in books of the sixteenth to eighteenth centuries. The projecting ends were either split, such as when used in stiff-bound vellum bindings with one half of the cores pulled through the joint (as when strips of vellum were used as a sewing support — and with a similar tendency to break down), or else the whole length of core projecting on either side of the spine was pasted inside or outside the cover — where in most cases it is still adhering today. Those cores formed by rolling strips of parchment together as a rule have broken one or even several times. For this treatment the material is, in fact, too hard, and cannot survive the movement of the spine as the book flexes when opened and closed.

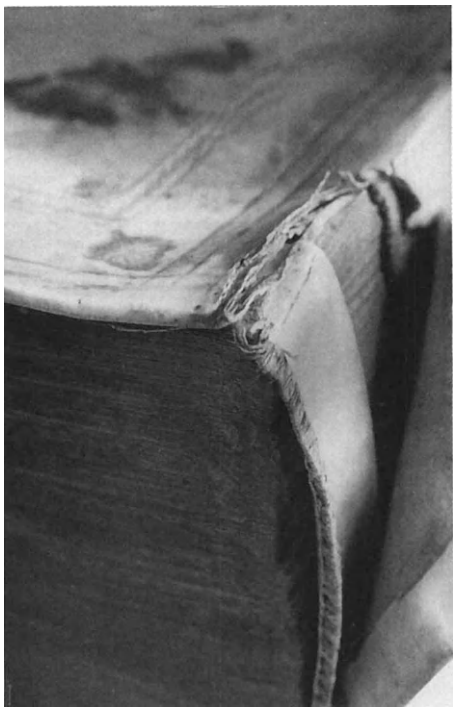


Figure 3.22.

Covering material: without boards

Without question, parchment or vellum is eminently suitable as a covering material for books of small format which are not too thick and need not have stiff boards *(Figure 3.23)*. Any study of limp vellum bindings reveals this very effectively. If occasionally a faulty example is met with, the cause may well lie in unsuitable procedures having been used, e.g. in the way in which the cover and pages have been put together. Adhesives were scarcely ever used for these flexible bindings.

Figure 3.23.

Covering material: with boards

The classic form of parchment binding in much of Europe from the sixteenth to the eighteenth centuries *(Figures 3.24* and *3.25)* has the following principal features: leaves with coloured edges; hollow back: bands pulled through; with or without fore-edge yaps: the covers half flexible pulp or pasteboards — to be held closed by ties made out of cloth or leather. The state of preservation of this type can, generally speaking, be either very good or very bad, depending on external factors such as the use or method and conditions of storage. Cases are also known of parchment suffering because of the way it was treated on book-making operations. An example is when parchment ultimately becomes as fragile as glass following the application of a layer of lime to the flesh side to make the skin appear as light as possible. However, many bindings of this style

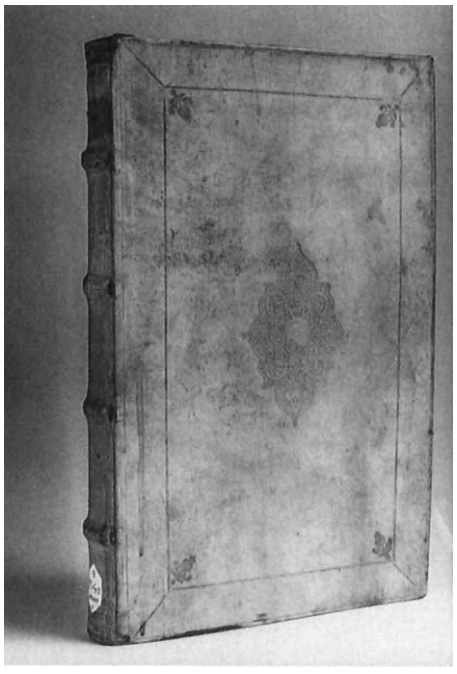


Figure 3.24.

are in an excellent state of preservation. In the Duke August Library, Wolfenbüttel, we have come across books in which the parchment has worked over the spine with double raised cords and firmly pasted with the joint in the Freench manner, and they are still in perfect condition.

The bookbinder of the end of the fifteenth century who used parchment to cover printed books in wooden boards was certainly both an optimist and a parchment fan, but his optimism was justified.

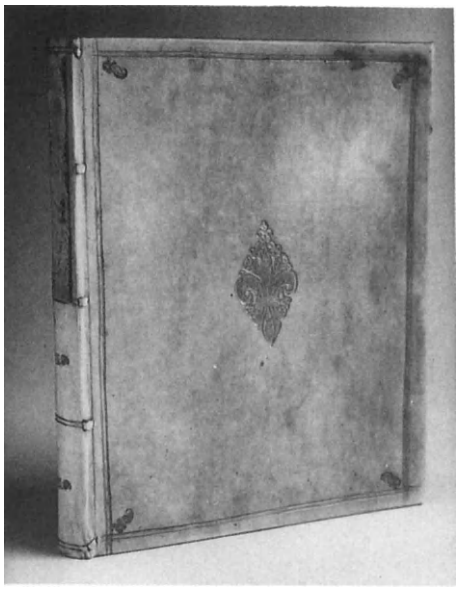


Figure 3.25.

Labels

Parchment is, of course, particularly suitable for labels, whether they are written on by hand or tooled *(Figure 3.26)*.

Figure 3.26.

As reinforcement for leather clasp strips

The leather strips with which the metal parts of clasp systems were fastened to the boards were sometimes reinforced on the inside with strips of parchment *(Figure 3.27)*. It has been observed that the parchment goes on holding the clasp, even if the leather has already broken.

The above historical digression has been deliberately placed as the focal point of remarks on vellum-leaved books, even though in so doing there is a risk of being numbered among the disciples of the medieval parchment fan referred to above. But to repeat the intention: to present a basic picture of the varieties of ways in which parchment was used in book-making and to help stimulate a greater use of this material in the many ways open to contemporary book restorers. (Every case, of course, will demand its own particular procedure.)

An essential difference between a paper and a vellum-leaved book as regards binding technique is the treatment of the spine. A vellum-leaved book, sewn on double cords, glued up, lined and covered

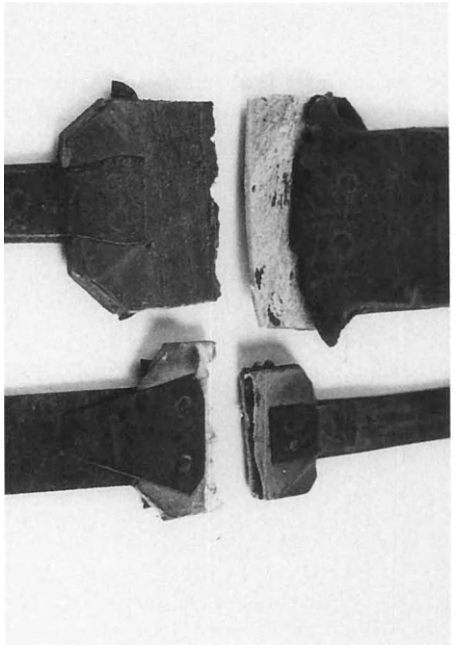


Figure 3.27.

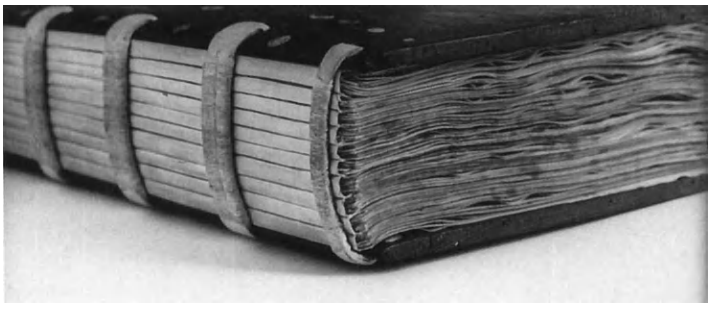
with leather, often suffers the following damage — the leaves, radiating out from the spine, have become heavily cockled with distortion over their whole area and deformed in such a way that the boards scarcely can be opened and the individual leaves cannot be turned over.

The cause of this problem lies in the material itself and is basically simple: parchment or vellum has the property of reacting by stretching or shrinking in response to variations in humidity. On the spine of such a book, however, the leaves are held as in a vice by the combination of the sewing, the adhesive and the covering, and are thus unable to respond dimensionally to moisture levels with the same freedom as the less-restrained areas of the leaves away from the spine. To prevent the creation of such problems for the future, one should proceed differently, as it is impossible to change the specific qualities of parchment itself.

There are technical solutions which can alleviate this problem after the vellum book leaves have been cleaned, mended and flattened as customary. At the sewing stage a piece of parchment can be bound in, folded backwards and forwards in 10 mm widths between the gatherings, so that their spine folds are wrapped in a zig-zag of new parchment *(Figure 3.28)*. In this way two things can be achieved: (1) the leaves, within certain limits, are able to move freely across or up and down the spine; (2) a greater degree of swelling is obtained — which is most important. Sewing using this technique is easier if a sewing frame is not used. After sewing the spine can be further worked as usual or one can dispense with spine lining and covering completely. The latter solution is preferable, especially when it is no longer clear from the old binding with what leather, if any, the volume was originally covered. The use of the zig-zag guard, commonly employed in the Duke August Library, has achieved much success, particularly when it is realized how easily books bound with such a structure can be opened for display and the taking of photographs.

The question of storage also needs careful consideration. Whenever asked about the storage of vellum-leaved books, one can only recommend the making of a good adequate binding and box tailored to the individual needs of each volume. Whoever, alongside the practice of book restoration, studies the histories and techniques of historical bindings, knows how much depends on each and every part of the process and on the materials used. With vellum-leaved books it is much more important than it is for incunables and early imprints on paper that the leaves be lightly but constantly pressed together. In the case of books with wooden boards, this is achieved through the fitting of clasps and in the case of books in paste-boards, through ties. If the book is also housed in an appropriately designed and well-constructed box or slipcase, then already essential criteria for good storage have been fulfilled.

Figure 3.28.



Besides the volume's binding and boxing, the second major requirement for good storage is, of course, a suitable immediate environment — above all, climatic conditions suited to the needs of parchment artifacts. It is generally known what are the devastating effects suffered by parchment as a writing or binding material from temperatures and relative humidities which are too high or too low or which fluctuate widely and rapidly. The careless attitudes towards the material under discussion which are occasionally encountered in bookbinders and librarians are most characterized by the lack of awareness of the deleterious effects of adverse environments. Data are available in the professional literature. However, although one can often find specified figures for relative humidity and temperature levels considered optimum for parchment and vellum, it seems more important in practice to be able to control the climate to within a certain range. This is a more reasonable approach, given the enormous expense of creating precisely controllable ideal environments in old library buildings. An extensive range of secondary literature regarding environmental monitoring and control and on the dangers of unsuitable climatic conditions exists. Not only may parchment and vellum as a text support and binding material be in jeopardy but also the writing and image layers (e.g. decorated initials and miniatures) may be seriously affected both directly and indirectly (through dimensional instability and deterioration of the parchment support).

The ideal exhibition case for vellum-leaved books demands a number of characteristics, some of which are difficult to achieve in practice. An airtight show case is difficult to manufacture and the objects for display cannot be readily be exchanged. For normal cases, therefore, one envisages a show-case which is sufficiently airtight to keep out the dust, but which at the same time allows an appreciable through flow of air. To facilitate air flow a hole should be cut out beneath the case with a diameter of 50 mm for every cubic metre within the case. The resulting change of air between the interior of the display case and its surroundings, resulting naturally from variations in temperature and baraometric pressure, occurs at the rate of about five complete changes a year. Specific atmospheric impurities have, of course, to be filtered out. This is achieved by providing the opening with glass fibre filter papers and activated carbon filters. Organic, hygroscopic substances used in the construction of the display case and its fittings can help to stabilize its internal climate. If a constant, predetermined humidity is desired for individual objects, certain salt solutions can be placed in shallow dishes within the case.

Correct display lighting is also essential. To prevent the show case from heating up, the source(s) of light should be located outside the case, preferably from above, rather than within it. Direct sunlight or spotlights, which can significantly increase the temperature inside the case, are dangerous. The best means of illumination are luminescent tubes with a low ultra-violet yield, so that colours and inks will not fade, and exhibition cases that have a lighting level of 50 lux.

Provision should also be made for the correct support structures for the display of books within the case. These should be tailored (e.g. from Perspex) to correctly support the individual book in whatever position, horizontal or sloping, etc. it is to be safely displayed.

Despite all the technical and physical factors which can affect the preservation of a book, one should not allow oneself to forget that man himself is still paradoxically, as always, the greatest enemy of books.

Acknowledgement

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4.1

Book Conservation

4.1.1 Priorities: a bibliographer's view

David F. Foxon

Bibliographical analysis depends on using evidence preserved in copies of a book to demonstrate how it was produced, but many sorts of vital evidence can be obliterated by conventional methods of repair or rebinding. Librarians and collectors have accepted the high-class trade bindings of the late nineteenth century as the norm without recognizing the extent to which they destroy evidence and are themselves unsatisfactory for their purpose. More flexible bindings which do not hide the construction of a book, like English limp vellum bindings of the sixteenth and seventeenth centuries, show the bibliographer all he or she wants to see and at the same time can be almost indestructible.

Bibliography has been defined as a study of the book as a physical object, and the bibliographer is essentially a detective using the clues a book provides to establish in precise detail how it was printed — and sometimes, where, when and by whom. Some of these clues, such as the type-face which is used, are indestructible, but others can be obliterated as easily as the clues to a crime. Let us start by giving some examples of the sort of evidence the bibliographer looks for, and how it can be destroyed by repair or rebinding.

The sheets from which books are constructed are printed on both sides, but one side has to be printed before the other. The bibliographer wants to know which side was printed first: the outer forme, which includes the pages on the outside of each section, or the inner forme. Early printing was always done on damped paper backed by felt blankets, so that each piece of type was pressed deep into the paper as though it was embossed; when both sides have been freshly printed it is easy to see which of these impressions was made last. The first job for bookbinders was to beat the folded sheets with a heavy hammer to reduce this unevenness, and then to press them.[1] Despite these processes, traces of the impression remain, giving the page a different appearance from the flatness of lithographic printing; often by careful inspection a bibliographer can still tell which side of the sheet was printed last, and thus trace one step in the order of formes by which the book was printed. But in the area where modern British and American bibliographers have been most active, the plays of Shakespeare and his contemporaries, almost every surviving quarto has been rebound in the last couple of centuries, and by overpressing, particularly of dampened paper, in the bindery this evidence has been completely destroyed.

Another feature of book production, particularly common in the eighteenth century, was the printing of cancel leaves to replace those originally printed when they contained errors of fact or judgement. The normal procedure for the binder was to cut away the offending leaf so that it left a stub at least half a centimetre wide; the replacement could be pasted to this stub, but more often it was folded so that it, too, had a stub which passed round the back of the section and was held in position by the sewing. When cancels have been made in this way they can easily and quickly be identified by the bibliographer, but more modern binders have put neatness above all things and removed the stubs, relying on tipping-in the leaves with paste or

overcasting the section; not only is the evidence destroyed, but the construction of the book is weakened. Often, if the watermarks in the paper fall conveniently, the bibliographer can still detect the cancels, but his task is made much harder.

It is not only the printing of a book that interests the bibliographer — he may want to know where a book was bound, since (for example) copies of books printed in one country but bound at the same period in another may provide important evidence for the international trade in books. Here the evidence of watermarks in the endpapers may be important, but binders and restorers have little regard for endpapers; they remove them, replace them, or paste new ones over the old, destroying this and many other forms of evidence.

Our last example is the most trivial but no less annoying. For an earlier generation of collectors and bibliographers one of the main criteria in the choice of a copy was its size, how little it had been cut down in the past; and before a copy was sent to the binder, the corner of one leaf would be folded down so that the owner could see that the binder had not cut away more than was absolutely necessary. (The French call this *epreuve de marges*). Sometimes, it seems the corner of a leaf was turned down by accident; but however it happened, this uncut corner shows how big the book was before it was bound, and if one is lucky it may show the deckled edge of the original sheet and help the bibliographer to establish the size of the sheet on which the book was printed. Yet some modern binders in the cause of neatness trim these corners away and destroy the evidence — what is worse, librarians have been known to do this too.

These are just a few of the sorts of bibliographical evidence that may be destroyed when a book is repaired or rebound, and we cannot know what else may be found to be of value as evidence in the future. It is not just a simple matter of avoiding such obvious pitfalls as we have detailed; even with the best intentions, any rebinding must destroy vital evidence of a book's original condition, and repair can hardly avoid doing some harm. It is admirable that some modern binders record details of how a book was originally constructed and what they themselves have done, but it is no substitute for being able to see the original binding oneself. In the same way it is good when libraries make bibliographical descriptions of books while they are being rebound, but it is idle to pretend that they will tell a future bibliographer all he wants to know. For the bibliographer, perversely enough, certain sorts of damage are a positive advantage when they help him to see the structure of a book which is normally concealed by the binding. The author's greatest bibliographical ambition at present is to find a copy of the second volume of Pope's *Works* of 1735 which is falling to pieces, for it was put together largely from sheets printed up to two years in advance, but mixed with revised sections and cancels, many of which cannot easily be distinguished by watermark evidence. Indeed, from the bibliographer's point of view the perfect conservation is simply to have a box made for the damaged book — and then stop other people using it and doing damage of the wrong sort.

This is not a solution which appeals to the librarian, who wants books that will sit neatly on his shelves and which can be issued to readers with the minimum of special treatment, but there is no way in which he can avoid his duty as the custodian of evidence. How far he can fulfil that duty may depend on how a given book is likely to be used: a reference book may need to be rebound, whereas a book for occasional reading can be repaired, and one intended for research kept in a box. Nevertheless very difficult decisions are involved and compromises are inevitable, and we must be grateful that librarians are increasingly thinking about this problem; in the past they have too often accepted the conventional solution — just as we all tend to do every day. We see what we expect to see, and do not question whether it is right or wrong. For the rest of this paper we will look at the problem of rebinding, which in the past was the librarian's normal cure for almost any book in need of repair; not only was it the accepted solution, but the sort of binding chosen was that which was normal in the trade rather than that which was best for the purpose.

A good example of how we can be blinded by the conventional is presented by the purchase of the Ashley Library by the British Museum after the death of its collector, the infamous T. J. Wise. One of the reasons given for its purchase was that the Museum copies of early plays were worn and dirty and unsuitable for exhibition, whereas those in the Ashley Library were near-perfect examples. We had occasion to make careful comparisons between them when trying to identify the leaves which Wise had stolen from the Museum in order to perfect his own imperfect copies; and the truth was very different. The Museum copies which had been plundered were mainly from the Garrick collection, and Garrick, in true eighteenth-century fashion, had sought the largest copies he could find; they were usually a good deal larger than Wise could find a century or more later. Originally Garrick had them bound together in thick volumes, which the Museum broke up to avoid unnecessary handling (carefully preserving the original end papers which

listed the contents of each volume); but the Museum binders merely cased the individual plays in half-morocco without resewing or pressing them. As a result, though they have occasional stains or foxing, the paper has its natural texture and colour (sometimes a fair white, sometimes a dirty grey) with crisp impressions of the type. By contrast, Wise's copies, elegantly bound by Rivière, have had the paper bleached, sized, tinted with cold tea to an 'antique' colour never seen in reality, and heavily pressed so that the final page looks like a rather bad facsimile. What is worse from the librarian's point of view, much of the natural strength of the paper has been destroyed by this process and the leaves feel brittle to the touch as if they were only held together by the size.[2] The point is that early in this century a binding by Rivière was accepted by English and American collectors as the best there was, and no-one thought to question its durability, or whether the book it contained looked like the real thing, let alone how well bibliographical evidence was preserved.[3] Librarians accepted the standards set by the collectors, and thought the Museum's collection greatly enriched by Wise's plays. The pendulum of taste was already swinging back to a desire for original condition in Wise's lifetime (he bought a first edition of *Paradise Lost* in its original binding, for example, in the '1920's'), and we can now see easily enough what an aberration this fashion was. We wonder, though, what we are blind to at present. It is only comparatively recently that the late Bill Jackson, the greatest American rare-book librarian of the last generation, came to realize how much evidence was lost when pamphlet volumes were broken up and the contents bound separately so that each work could stand in its proper place on the shelves of the Houghton Library at Harvard — that was accepted American library practice.

To talk of Rivière is only to talk of the furthest development of the trade traditions of the nineteenth century, and the aims of that tradition are still potent: the desire to produce a tight, rigid binding that stands firm on the shelf and conceals the way it is constructed — no trace of sewing, no evidence of cancels. Even attempts to give library bindings strength ignored the natural construction of the book. Bernard Middleton described in 1963:

> An extremely strong endpaper which was adopted in the British Museum Bindery towards the end of the nineteenth century, and is still extensively used there in half-morocco bindings, involves overcasting a cloth joint on to the book after it has been sewn. This has the virtue of grading and spreading the strain among about three sections instead of the last one only.[4]

Fortunately this practice has been abandoned; the first section of the book used to be overcast, contrary to the natural way of sewing, and the total effect was to make the book very difficult to open.[5] Pity the poor bibliographer who wants to see whether the title of such a book is a cancel — he tries to ease the binding open to see if there are traces of a stub beside it, and suddenly there is a horrid moment when the overcast stitches tear out of the title or half-title. That leaves an embarrassed and frustrated bibliographer, and a book which is now either in danger of losing its title, or which has to go back to the bindery again.

The author was reared in a much better tradition, since he went to school in Bath, where the library's binding was done by the local firm of Chivers. Cedric Chivers (1853-1929) devoted a lot of thought and research to finding sound materials and methods for library binding, and Douglas Cockerell, who gets most of the credit for the 1905 'library' specifications, was clearly much influenced by him; his ideas went well with the concept of fitness for purpose that Cockerell had learnt from the Arts and Crafts movement. The reader will be familiar with those solid library bindings, and we are not suggesting they are appropriate for the purposes we are considering here; but their refusal to hide sensible construction for the sake of glossy appearance is relevant to our purpose. We are thinking particularly of the sewn-in endpaper with a stout coloured cloth joint: there is no attempt to hide the cloth reinforcement, which is a decorative feature against which one can see the linen thread which holds it to the rest of the book. To sew the endpapers through the fold in the same way as the other sections of the book is the only sound and logical method of construction, and all binding was done in this way until the reprehensible practice of pasting-in endpapers became normal in the early nineteenth century. But the use of cloth reinforcement of the joint to stop the thread pulling through the paper at this, the point of maximum stress, is also a throw-back to the normal sixteenth-century practice of placing a strip cut from a vellum manuscript within the fold to take the strain — also without the least attempt at concealment. (In the same way Chivers used unconcealed cloth guards for the inside and outside of the end sections, just as vellum guards were used inside each section when books were first bound from paper instead of vellum.)

This honesty about the way a book is constructed is just what the bibliographer seeks; the English limp vellum bindings of the sixteenth and seventeenth centuries are ideal, above all, because they have loose backs and open so easily that everything can

be seen. Not only can one see the sewing in the centre of each gathering and any cancels that may be present, but almost the whole of the watermark can be seen against the light; in quartos and octavos the watermark lies in the fold of the paper and is more or less obscured in normal bindings. We are learning more and more about watermarks and their importance as bibliographical evidence, so this ability to see them clearly is of great importance.

These limp vellum bindings are not very well known, and we should perhaps say a few words about their construction — without claiming to have made a proper study of them. Continental vellum bindings of this period are often made with hard backs: that is, vellum is glued to the back of the sewn sections, with the result that the book is very difficult to open. An alternative Continental practice was to glue strips of vellum over the spine between the thongs on which the book was sewn, but to leave the back free: that gives us a precursor of the hollow back that became popular in the nineteenth century, but it is still difficult to open these volumes. The English bindings, by contrast, are very flexible; indeed, Bernard Middleton may well be right in describing them as casings rather than bindings,[6] since the cover was made separately and attached to the book as the final operation, rather than built up on the book. The normal construction seems to have been that the book, including the endpapers (which were sometimes reinforced with a strip of vellum), was sewn on raised thongs of tawed leather or slips of vellum. The spine was sometimes gently rounded and usually lightly glued, though some open so very easily that one wonders whether, like primitive Coptic bindings, they are held together merely by the sewing, perhaps aided with a little paste. The thongs or slips were then laced through slits in the joints of the vellum case, and the book was complete: normally the endpapers were not pasted down to the inside of the covers.[7]

This style is not only the bibliographer's delight; it should please the librarian too, since it seems almost indestructible, particularly at the joints of the covers where leather bindings all fail sooner or later.[8] (Of course, the bibliographer is happy about that as well, since it means that he can pry as much as he likes without doing any damage.) The only weak point is the lacing of thongs into the covers, since this takes all the strain, especially when the back of the book is more flexible than the vellum spine; the problem seems only to arise when the book is sewn on leather thongs rather than vellum slips, probably because leather is intrinsically weaker than vellum, and because the edges of the slots in the vellum covers cut into the softer leather of the thongs. It is true that larger volumes — whether larger means a tall folio, or a fat octavo — have a floppy feel, especially by contrast with hard-backed leather bindings; this is because the binding and the contents are not pulling against one another, which is one of the secrets of their strength, but it does mean that the foot of the leaves tends to rest on the shelf rather than hang in the air. (The covers of early bindings were always flush with the leaves, and we have wondered whether the 'squares' to which we are accustomed have advantages which outweigh the strain they put on the spine of a book; almost all the larger books the author owns sag on to the shelf despite them.) Many of these bindings were made with a couple of ties at the fore-edge so that the parcel could be tied up firmly: unfortunately these, whether they were leather thongs or silk ribbons, have almost always worn away.

We are not arguing that every book that has to be rebound should be put into limp vellum. The argument is more general: that these apparently flimsy bindings have survived a great deal better than more modern, more rigid, and apparently stronger bindings. Generations of binders, collectors, and librarians have blindly followed fashion instead of searching for the best solutions; as a result millions of old books have have been rebound in such a way that bibliographical evidence has been destroyed — and many now need to be rebound once more. We should recognize that a properly sewn book is structurally sound in itself; it is the stresses imposed by tight backs (or, indeed, hollow backs when heavily glued and lined) that lead to breakdowns. It is more than chance that this style of binding is ideal for the bibliographer; it is exactly because it relies on the natural strength of a book's construction and tries to hide nothing that both bibliographer and librarian are well served. (There is an exact parallel with the treatment of cancels: taking a stub around the back of a section so that it is held by the sewing is the only reliable way of securing it; it also reveals all to the bibliographer.) When books have to be repaired or rebound, let us seek methods that give strength with flexiblity and not sacrifice evidence to conventional ideas of neatness and propriety.

Notes and References

1. The question was raised in conference discussion whether it was the type area of the sheets that was beaten or the margins. William Savage in his *Dictionary of the art of printing*, London, 1841, p. 439, discusses the order of formes, and says it is usual to print the inner

forme first. 'An old reason for this practice is, that it is advantageous to the bookbinders in beating the book, preparatory to binding it; as the indentations of the types face one another, and are more easily made smooth; but the indentations would face each other equally if the usual order of working the forms were reversed.' Though the traditional fallacy is exposed by Savage, he has no doubt that the purpose of beating was to smooth the type area.

2. The author is reminded of his embarrassment when he worked in the Pierpont Morgan Library on some of John Wesley's little duodecimo collections of hymns, pamphlets of twelve or twenty-four pages which had been bound by Rivière in calf which had been pared paper-thin. Every time he opened one of them — no doubt the first person to do so for many years — the upper cover came away in his hand. The staff were very understanding, but he still feels disinclined to go back to that library.
3. The bibliographical naivety of collectors like Wise is astonishing. He often had two copies of an early play bound, one for himself and one for his friend, customer, and dupe, J. H. Wrenn of Chicago; It was common for him to exchange leaves between the two copies, destroying the bibliographical integrity of both. Often his aim was clearly to transfer unsatisfactory leaves to Wrenn's copy. On one occasion he unwittingly gave Wrenn the rare uncancelled leaf E2 in Ben Jonson's *The Alchemist,* (1612), because it was disfigured by the slit with which printers usually warned binders that a leaf had to be replaced with a cancel.
4. Middleton, B. C., (1963). *A History of English Craft Bookbinding Technique,* New York and London, 47n.
5. The author is told that there are occasions when overcasting is expedient, and that it can produce acceptable results if it is properly done, but it inevitably frustrates the bibliographer who wants to know which leaves are conjugate with one another. On the other hand, the use of a conventional sewing machine, producing a row of perforations along which to tear out the page, is unforgivable.
6. Middleton (1963), *op. cit.,* 111, n.4; 141-142.
7. A very similar binding was used for presentation copies of pamphlets in the late seventeenth and early eighteenth century. Whereas pamphlets were normally stitched or stabbed through the thickness of the pamphlet, fine-paper copies were sewn, including thick endpapers. Marbled paper was then pasted to the endpapers, but left unattached at the spine so that it formed a loose back. Usually the edges were cut, and often gilded.
8. Christopher Clarkson has made an extensive study of this subject, as yet unpublished in its entirety, some aspects of which appeared in: Clarkson, C., *'Limp vellum binding — and its potential as a conservation type structure for the rebinding of early printed books — a break with 19th and 20th century rebinding attitudes and practices',* ICOM Committee for Conservation 4th Triennial Meeting, Venice 1975, 15/3, 1-15. The author was entirely ignorant of his work when he wrote these notes.

4.1.2 Conservation priorities: a book conservator's view

Dag-Ernst Petersen

The topic of priorities in book conservation tempts one to ask, what is to have precedence over what? Such terms as invisible, tooled, coloured aesthetic, durable, reversible, original, facsimile, reconstruction, falsification all come into play. However, if you analyse them and find out what they have in common, you will find at least three closely connected concepts: technique, materials and aesthetics. To sort out the customary priorities between these three concepts is a simple matter if you first ask the question 'who owns the book which is to be restored?' Is it a public library, a private collector or an antiquarian bookseller?

The most important thing for the bookseller — besides the value of the book — is that it should look good after it is repaired, so that the potential purchaser has the impression that the binding is genuinely old and undamaged. Invisible repair, colouring and filling out missing portions of the text are considered of greater importance than the durability of the repairs actually carried out. The repair work will be judged successful if the book looks as if it has never been repaired.

The demands of the private collector are very different. For him, it is important to keep as much as possible of the original material of the book, so as not to disturb the character of the book. The volume is allowed to look used and fragile, that is, to look its age. If individual parts have to be replaced, great care must be taken in choosing the right material. It must be as close to the original in appearance as possible, and sometimes may even be old material itself.

When working for a public library, the priority in book conservation has to be first the techniques used in the construction of the binding, secondly, the choice of material and thirdly, the aesthetic consequences of the chosen method of repair. To this end, we will give some examples of what we understand by these concepts, how they work together in book restoration, and how they can cause conflicts in practice. In doing so, we also explain our own attitudes to the question of priorities in book conservation.

When one first considers the subject of priorities in book conservation the question which immediately springs to mind is — what exactly is to have the priority over what? Our answer to this is to describe the path taken when one restores a book, a path dictated by needs such as durability, strength, reversibility, tooling, colouring or invisibility, and involving aesthetic judgement on originality, reconstruction, imitation and falsification. At this point we would just like to mention that we are discussing these concepts basically with regard to the restoration of bookbindings, for paper restoration does not come into the scope of this paper. When one analyses these headings and arranges them according to their basic similarities, three major concerns may be determined:

Technique;
Material;
Aesthetics.

If one then examines these points more closely their interrelationship is immediately apparent. The

strength, durability and functional value of the binding are all dependent on the technique, or binding structure. The choice of material influences first, the durability and functional value of the old book, and secondly, its aesthetic impression and third, its authenticity.

The aesthetic value of the finished work arises from the choice of materials, the workmanship and detailing, from the inner logic expressed in the technical execution and from a minimum of individual creativity, which must always remain subordinate to the original book. This aesthetic value, which may even pertain to an old book in a damaged condition, is totally destroyed by poor craftsmanship.

As one can see, these principles are closely connected — indeed, from a theoretical point of view they are inseparable. Some readers may well ask why we have separated them at all, but in practice the restorer does have his own priorities, which decisively influence the results of his work. The question which now arises is what circumstances determine the order of these three factors? This question is basically answered if one goes on to ask who owns the book which is to be repaired — a public library, a private collector or an antiquarian bookseller. Let us explain these alternatives in greater depth.

Apart from the value of the book, the antiquarian bookseller is most interested in its visual impression. Every bookseller wishes to offer for sale a valuable old book in its original binding and in good condition. If a volume is damaged, he takes it to the restorer: in this case the inconspicuousness of the repair, the restoration of the decoration or even of parts of the text have precedence over the durability and thoroughness of the restoration. We hardly need to mention that such compromises are made in order to save money. A thorough restoration always takes more time and is naturally more expensive. Several years ago a dealer handed the author a leather-bound book and asked him to ascertain how the cover was fastened to the joint, as the join was almost imperceptible. After he opened the cover a few times it fell off, and he could easily see how it had been made — with an ample quantity of Japanese paper, glue and colour! That is, of course, an extreme example, and not to be taken as characteristic of either profession.

Secondly, for the private collector, the primary consideration is the originality or authenticity of the book. He likes to see as much as possible of its historical substance retained, so that the special characteristics of the volume are preserved. We know bibliophiles who no longer allow books in their collections to be restored for fear that the authenticity of the book may thereby be lost. For them it is perfectly acceptable that their books look old, used and fragile.

If something is to be improved or restored the choice of material is of the greatest importance. It must come as close as possible to the original and occasionally old materials may be used in the process. For the bibliophile, who treats his collection with utmost care, the firmness of the binding is of secondary importance.

Thirdly, in a public library the books are not purely cultural treasures or collector's pieces but, above all, a source of information for the reader, which often leads to an intensive and unsparing use in the reading room. A different procedure should therefore be employed here, one which we are able to practise daily in the Herzog August Bibliothek. Here great importance is laid on the high quality of the binding techniques involved, which, coupled with a careful choice of materials, leads to an aesthetically pleasing finished produce. Only when we observe the factors in the order described above do we attain a strong, durable binding which can carry out the following functions: first, to make the contents of the book easily accessible to the reader — and second, to protect the contents of the book. However, this does not mean that the old binding components are removed and replaced by new ones, purely because they are old and perhaps loose. Only those elements which strained when in use are renewed with modern materials of a similar kind, should their poor condition call for this. At every stage of restoration we consider whether the present condition can be kept or whether it must be improved in order to increase sturdiness. Such considerations usually conflict with the fundamental principle of altering as little as possible of the original substance of the book. For example, if the book was bound in sheepskin we use goatskin, which is very similar in appearance, only more durable, or in the case of a medieval binding with wooden boards, if the inner joint was lined with paper we would use leather in the restoration. We always decide in favour of durability.

The essential parts of an old binding which may have to be replaced, for example the head band, leather spine, bands or back linings, are not thrown away, but are documented and carefully preserved in a collection of old binding fragments. As a matter of principle, every alteration or operation is documented in the restorer's report.

In the Herzog August Bibliothek aesthetic considerations have always been of special importance and have naturally included the restored book. For instance, a new leather will be dyed so that it both matches the old leather but still keeps its new

appearance. Missing parts in the bookbinding decoration, even if these are only lines, are on principle never restored. Here our practise differs fundamentally from book restoration in France. We have restored books for a public library in Paris where the decoration was imitated by tools specially engraved for the purpose.

The scope for personal initiative on the part of the restorer remains extremely limited: on the one hand, he is not allowed to be creative, and on the other, he is forbidden to imitate the old binding, whilst falsification is entirely out of the question.

However, before we start to discuss the principles rather than the priorities of book restoration, or even become tempted to reformulate the Code of Ethics we will bring this paper to a close.

Acknowledgement

Translation from German into English by Sarah Dewhirst and largely corrected by NWMP.

4.1.3 Conservation priorities: a bookseller's view

John Maggs

The antiquarian bookseller who is a genuine bibliophile has, in the nature of his occupation, a number of dilemmas to face concerning the conservation of works in his custody, temporary or otherwise — balancing his concern for preserving the historicity of his material in a great range of states and forms, against the high costs of responsibly repairing, binding or boxing, book trade market considerations, and the bibliocidal tendencies of some clients (or would be clients). A gathering of the author's thoughts and experiences in these areas is briefly narrated.

Whether one likes it or not, the bookseller must constantly keep an eye on costs and cash flow, and as conservation is expensive, it is better to try to avoid the problem by buying stock which is already in good order. Although many of the books now appearing at Sotheby's are in poor condition, it is still possible to be selective and to concentrate on those in fine state, and the extra cost may well be considerably less than the cost of repair. But when buying a library in bulk, many items will be included which need attention, and one is very well aware that the appropriate facilities for repair may not be readily available where the eventual customer lives. The cost of repair has to be built into the price, and should the item be delayed for years at the binders, it may very well work out much higher than had been anticipated. But there is little chance that there will ever be a uniform approach to standards of conservation, and one often wishes that the previous owner had left the book alone. We declined an important book recently because of the activities of an economical cobbler.

A good bookseller is expected to carry a wide range of stock, and the cost of storage space demands inexpensive premises, which are unlikely to be ideal. Fortunately, the British climate is kind to paper, and provided the storage area is not actually damp, experience indicates that books can keep very much better in the basement of such a bookshop as ours than they may do in an overheated modern library building. Sometimes stock arrives in single volumes, and is therefore easy to classify and store, but when a large collection arrives in bulk, there are very substantial problems. One tends to stack in cartons, and no conservator should see some of our stacks. In this connection we frequently feel the need for special lightweight, but durable, crates which both nest and stack, and weigh no more than 25 kg when packed — if they are heavier, they are more likely to be dropped.

Pamphlets are one of the most worrying areas. These frequently arrive in good bindings provided by an intelligent librarian a century or more ago, but who, for economy, put batches of miscellaneous pamphlets together. There is little chance of finding a buyer who would want them in the same random order, and so they are almost invariably extracted and housed in envelopes, which are preferably slit along one side so as to reduce the risk of damage when inserting. The original owner will have his bookplate at the front of each volume, and some of the pamphlets might have presentation inscriptions from their anonymous author. However, by disbinding, these indications of provenance will be

lost. We try to note the name on each separate item, and we wish we could make it a rule. We have even known cases where a map has been separated from its correct place at the end of one pamphlet and filed away with the next. It seems strange to think of a bookseller as a guardian of morals, but we can think of examples where one loses a sale in order to keep a collection intact. Ideally, disbound pamphlets should be bound separately — suitably lettered up the spine for easy identification — while unbound pamphlets should be boxed. The author's father could get Rivière to bind in quarter morocco, with 1 point lettering, at 3s. 6d. each, but it is out of the question to spend £10 on binding a pamphlet worth, say, £15. And boxing is strictly uneconomic for anything below, say, £50. Perhaps ordinary box files are the answer — however dull they may appear.

Thoughts on disbinding easily lead us to the distressing subject of map collecting. When retained in their massive bindings, maps have survived quite safely from 1482 or later, but when removed, deterioration can set in rapidly. A careful map dealer will not display his stock before every map has been mounted (in acid-free board, of course), although framing might make the complete article liable to VAT (Value Added Tax). It will then be reasonably safe from creasing and finger marks, but exposure to light will certainly begin the process of destruction. The author recalls that his childhood home was decorated with framed mezzotints which have since found their way into the attic via the spare bedroom, and they are unlikely to emerge without broken glass and consequent ruination. Framed maps came into popularity only twenty or thirty years ago, and we feel certain that the fashion will someday give way to something else — perhaps blank walls — and so we can predict the eventual destruction of what once were fine books. We come across the attitude sometimes that because an architect has paid for a Popple map of America, he is entitled to glue it to the wall in the lobby of his new skyscraper. Again, the bookseller can find himself as a sort of self-appointed conservator, and on occasion, this can lead to mild blackmail from a keen salesman: 'Either you buy this superb atlas at once, or I shall be forced to sell it piecemeal to a queue of rich and enthusiastic collectors of separate maps — and the contemporary red morocco covers will find a ready market as blotters.' Restoration of volumes of maps or views can be heartbreaking when a buyer is obviously concerned only with the breakup value. The author recalls asking an American buyer of a Gould bird book for shipping instructions, and we were told to keep the covers and send the contents. The deal was cancelled and the book was eventually sold elsewhere.

A personal enthusiasm concerns books in original boards, uncut, and now that we have invested some of the firm's capital in a roomful, We can begin to evaluate the problems — and they are terrifying. Most are suffering damage to some extent, and in the few examples where we have attempted repairs, the results generally appear less and less attractive. Few binders seem to have suitable paper for rebacking, and printing paper labels in true period style appears to be an impossibility. We are at the stage of believing that all restoration should be sympathetic, and while not being fraudulent, should, nevertheless, be inconspicuous. And yet in another area, we are still unable to forgive Viollet le Duc for his work at Carcassone. So perhaps, ideally, all our books in original boards should be preserved in boxes, as they are — and if the paper is peeling from the cover of an early nineteenth century American volume, so as to show the wooden boards, so much the better. If stitching happens to be loose, then it makes it so much the easier to see the arrangement of the sheets.

Then there is the little matter of the education of the client, who may be a most successful oilman, but a newcomer to the world of books. It is both a privilege and a responsibility if one happens to be the first bookseller to be in touch with an aspiring collector. We like the 'soft sell' which builds up over years, but in a recent case, we have been outclassed by a more energetic dealer — the client's marriage was less stable than we had imagined, and the settlement will put paid to book buying for some time.

The care of autographs and documents presents fewer problems to the dealer. They store easily in paper folders, and they are usually marketed through catalogues. The collector can keep his holdings in normal steel filing cabinets, and only a few will resort to the disagreeable practice of exposing their treasures to full light. As regards repair of torn folds, ideally one would like the luxury of a Drescher job, but, as always, the cost element has to be considered. From the dealer's point of view any form of silking or laminating is unacceptable.

Perhaps we may be allowed to end with a short sermon. Booksellers, collectors, librarians and archivists may differ on any aspect of our specialist area, but on one we must stand together — any of us can unwittingly assist thieves in what has become a major tax-free activity. Only recently the author has been involved in another case of stolen archives, and once again we are being asked to be discreet. We must not be ashamed to confess our short-

comings and, wherever possible, we must look to the police for help. But this involves helping them too, and the author is coming increasingly to the view that we must all investigate methods of secret markings, such as UVL stamps, so as to be able to make definite identifications when all other marks have been removed. We have just been faced with an Aladdin's cave of stolen books; it is infuriating to think that any which remain unclaimed may be returned eventually to the thief, who frequently receives only a suspended sentence.

4.1.4 Conservation priorities: a library conservator's view

Christopher Clarkson

While the staff of our great library and archive institutions struggle with their evergrowing dumps of books which simply cannot be used, their own administrations are probably still allowing acquisition funds to far outstrip preservation funds, encouraging poorly constructed and damaging exhibition display or doing nothing about stabilizing environmental conditions.

The changing use, indeed overuse, and shifting emphasis of library and archive materials in many subject areas do not help clear-cut decision making and balanced policies. But as the author travels around repositories, what he notices so often are wrong-headed policies developing, and programmes spawned out of panic. Clear-cut guide lines must be set out for the staff to see where they can make a positive contribution to their institution's preservation and conservation efforts.

Our major libraries have two basically separate functions; first a role as a very broad and up-to-date reference library, and second, as a museum of the book. In almost every case the economics, staff training and functions are directed towards the former role; the latter one is hardly acknowledged. Yet much of the nation's wealth and heritage is bound up in the library as museum , and although there are grey areas and overlapping areas between, surely it is not beyond man's wit to separate these two mainly dissimilar categories of the library's material. Each category requires staff with substantially different training, approach and equipment from the other. The present mixed situation can only lead to further confusion of priorities and damage to the books.

To separate obviously valuable books and place them in a room or building which is environmentally stable and secure, housing it with specially designed furniture is, of course an idea which has been around for many years, particularly in America. Perhaps all we are saying is that this idea should be greatly expanded to cover far more of a repository's material and be linked to a system of priorities where *preservation* comes first and casual and individual use of the item comes second. Such a shift in policy would help the material to last a little longer, making its use less private and less likely to be used for purely egotistical reasons.

Many libraries are now acquiring sophisticated analytical equipment, which is a great boon to the modern researcher, but one must be conscious of the potential physical damage which can easily be caused to artifacts when such equipment is used in a non-laboratory environment and with untrained staff. Ultra-violet, beta radiography and microscope facilities may be fine but require specially designed reading examination rooms to cope safely and a skilled and knowledgeable staff qualified to aid and invigilate. Of course, the design of such reading facilities must include improved book handling such as increased use of horizontal shelving, wider tables and gentle book cradles of various designs instead of flat lecterns.

By *preservation* we mean prevention of damage, both physical and chemical. The word defines a subject which encompasses every facet of library life; it is in a real sense *The Library*. The most expensive cataloguing and retrieval systems, the most knowledgeable staff count for nothing if harm

comes to the library materials — *the information*, that is, both from the point of view of information contained, or, in the case of period materials, often the whole physical object itself or its associations. Preservation — or preventive medicine — is the concern of everyone who walks into, or works in, a library. As a conservator the author considers himself only as a small part of this huge subject.

We use the word *conservation* to refer to the specialized process of making safe, or to a certain degree usable, fragile period objects. At the same time it also encompasses the dispensing of knowledge and advice on the care of such objects. *Restoration* expresses rather extensive rebuilding and replacement by modern materials within a period object, catering for a future of more robust use. To generalize then, *restoration* implies major alterations, *conservation* minimal and *preservation* none. To clarify somewhat the grey area between restoration and conservation, we would say that a major difference is in *intention* and the greater skill and knowledge which is always required to achieve *the minimal necessary* or the simplest answers. In England, at least, there is a certain terminological confusion. For example, in the Civil Service a 'Restorer Grade' is higher than a 'Conservator Grade'. This is, of course, only a misuse if your standard of comparison is the way in which the words have been used during and since the pioneering days of our young profession and by its spokesman the International Institute for Conservation of Historic and Artistic Works (IIC), where *restoration* means major replacement. Analogous with this is the concept that such work can only possibly be an interpretation of the restorer's period or culture.

A codex book is an object constituted of multiple and separable components; gatherings, binding construction, metal furniture, fastenings, etc. Combined, these form numerous subtleties of historical interest and theoretical evidences, indicating period fashion and provenance; divided, they lose much of their meaning and power to conjure human thought. Bibliographical integrity is not something one can dismantle and recreate. Judged in this way, the integrity of the individual volume is only as strong as its most fragile or weakest part; as with a painting when only one colour may fade but the artist's intention is altered forever, leaving its integrity fragmented.

If left undisturbed, a text-block and its binding are of inestimable value to the development of bibliographical studies, while any encroachment by the restorer tends to lessen such value. Nonetheless, certain conservation and restoration activities often have to be carried out to ensure an object's stability and continued preservation. Here is the major dilemma.

However skilful and knowledgeable a conservator's work, one must accept that certain alterations of a period item will take place. The degree of alteration largely depends upon a conservator's judgement as to the future use and vulnerability of the book. Never judge a conservator's or binder's work without first taking into consideration his 'brief' and/or the institution's facilities, philosophy and policies. For example, one will not improve anything by criticizing a binder for excessive interference and unwarranted restoration, to the degree that he is only a reflection of the attitudes and toleration of the institution he works for. What we find to be the widest void in communication with custodians of library materials, except for a few who probably are in this audience today, is the complete lack of sympathy for the physical needs of the books in their custody. We probably all have our own pet examples of national treasures which have been permanently damaged by the recent growth of insane environmental conditions, loan exhibitions, practices used in facsimile photography, etc. The difference in aesthetics, connoisseurship, security, preservation and conservation quality between our major galleries and our major libraries is very startling. An object treasured in the first will often be totally disregarded in the second. One of our particular interests is English Romanesque bindings. We wonder if anyone realizes the destruction which has occurred to such bindings within the past twenty years, not simply through neglect or ignorance but often, it appears, through a wilful desire to make them conform to modern library practice. It is already clearly evident that the few bindings which are in museums or private collections are generally in a finer state of preservation. In discussing the situation with the longer serving members of stack staff, it is apparent that in English collections the increase in deterioration has accelerated phenomenally in the last two decades.

Why is this happening — over and above the absence of *preservation* as a leading factor in policy making within an institution and the pressures of a burgeoning readership? One has the situation that the staff and traditional library facilities cannot cope with the study of the book as a physical object. The sheer weight of present and growing interest in codicological and bibliographical studies has seemingly caught our repositories and training programmes off balance. As we walk around reading rooms we observe readers literally pulling library materials to pieces in their endeavour to understand the physical composition of a volume.

Such damage is now a daily occurrence. As a typical example — a few weeks ago a reader was observed holding a single leaf of a seventeeth-century Persian manuscript up to a window by its fore-edge, while the rest of the volume hung down without support. His incomprehension when we tried to explain the damage which could be caused was only countered by our own when he showed us his codicological report form; it was the most elaborate we have ever seen, consisting of 18 pages full of questions, all of which he said he answered himself. Some of them an extremely knowledgeable conservator and/or analytical chemist in a well equipped laboratory would be strained to answer correctly. Such naïveté may cause one to chuckle but this particular reader had been encouraged by his university tutor and gained a large grant to study particular manuscripts throughout Europe. What good are such amateur and private efforts, particularly when one considers the damage being done? How very irresponsible of university faculties and grant-awarding bodies to encourage such projects, without at least close collaboration with the various repositories.

Here again we have damage being done through people lacking what we can only think of calling *material awareness*. In the past, from the time of the Ancients, even up to some sixty years ago, man's close contact with natural materials formed a continuous link in the traditions of craftsmanship. As Dorothy Hartley explains superbly,[1] 'The mental strength of this Man was his earth-inspired commonsense. Much of our knowledge (on the other hand) is secondhand and our speech betrays us when we say "I know for a fact", by which we mean a small definite piece of knowledge. In contrast, all our basic man did know was "fact", and so his material knowledge went much deeper than ours. A modern woman sees a piece of linen, but the mediaeval woman saw through it to the flax fields, she smelt the reek of the retting ponds, she felt the hard rasp of the hackling, and she saw the soft sheen of the glossy flax. Man did not just see "leather", he saw the beast — perhaps one of his own — and knew the effort of slaughtering, liming and curing.'

As far as the understanding and responding to period materials and techniques goes the gap between today's conservators and those earlier craftsmen is surely large, but there must be some common ground by virtue of working with natural materials. But what common ground have modern administrative and library-trained personnel with such craftsmen. There reigns, in fact, complete incomprehension. Radical changes in training and outlook are necessary and must be achieved quickly.

Training of staff is fraught with difficulties. For example, in book binding alone, the current European conception of a bookbinding is misapplied by being imposed on pre-eighteenth-century European books or on books from alien cultures. The thoughtless application of late European bookbinding traditions has caused immense damage to cultural property throughout the world.

The development of guidelines for preservation, conservation and restoration are urgent, but information collected must be based upon sound research by the scientist, book conservator and scholar. This necessitates an interdisciplinary language, methodology and framework, which, because it must record and communicate such difficult concepts as material qualities and structural deviations, will require, over and above the basic language, other descriptive tools such as photography, samplers, diagrams and movie film. Once such a programme was undertaken one would then gradually see the development of a profession with a backup 'information bank', in this case one dealing with the book as a physical object. At the Bodleian Library, Oxford we wish to combine the reference library for physical book studies with that for conservation because they are one and the same subject, and place such a reference library at the hub of condition surveying and preparation for conservation. Correct interpretation of an item depends upon three specialists; the theoretician (art historian, curator, bibliographical scholar, etc.), the conservator, and the analytical chemist. Each is enriched by the other, all must be bound by similar ethical principles and each is very necessary for balanced preservation and conservation programmes.

In this gathering of knowledge, it becomes increasingly difficult for binders or conservators to anticipate what will be the most important aspects of any particular volume to future scholarship, and therefore it becomes correspondingly difficult to say what information must be available to conservators in order to make a professional judgement. As with any other art object, early books with their diverse materials and techniques used warrant careful, individual study and attention. We cannot simply turn to booksellers, collectors and librarians, for suitable guide lines and philosophy for, except in rare cases, they have been noted more for their business or administrative acumen than their historical and bibliographical sensitivity. Consequently books have often suffered from restoration and rebinding practices which were good for the former but bad for the latter. To such people the basic characteristic of a saleable or

useable book has been in the past as it is today — 'good' to 'excellent' condition. This attitude has led to the practice of 'tidying-up' an item and always with an eye towards the cheapest price for the work. Such policies are disastrous for our bibliographical heritage. Clients often turn to conservators as the experts, and as professionals it is surely our ethical responsibility to inform them clearly what standard of work is necessary, what repercussions it will have on the item, and the various possible alternatives which could be considered. It is vital that we create an awareness of the owner or custodian's role as a guardian of the item for the future benefit of all.

With period materials, refurbishing and rejuvenation along with education in handling and housekeeping and careful invigilation of readers must be promoted to major priorities. Research and development programmes should be directed more towards such areas than to restoration and rebinding.

In the present economic recessionary climate we cannot hope to have enough staff or training facilities to do anything which could be thought of as adequate.

We finish by listing a few of the systems which we are concerned with developing at the Bodleian Library at present. Over and above a stable and clean environment, physical protection of library and archive materials is very necessary. A comprehensive system of protective methods is required to cope with the diversity of problems. This will include commercially produced archive quality book boxes, four-flap folders and stiffened envelopes all ranging in correctly related dimensions matched to Occidental and Oriental book and paper sizes, and guard-books consisting of boxed fascicles where each of the single-section fascicles contains compensated support sheets to which single-leaf items are attached. Running alongside such commercially produced protection is an individually tailored boxing programme ranging from flap boxes through various designs and elaborations to book boxes for treasured items. Transit cases and crates are another category which caters for the movement of books from one building to the next. For loan exhibitions such cases must be even more elaborate in their specifications. The whole protection system must relate as closely as possible to an institution's bookstack sizes, display cases, wall frames, etc.

Reduction of costs by linked programmes (bulk buying) between libraries is a major consideration for economic reasons, and as an incentive to manufacturers to produce materials and equipment to specification, not only in areas such as archive storage boxes and guard book fascicles but also, for example, in book cradles, exhibition cradles, display cases, transit cases and horizontal shelving. Standardization of sizes between libraries and galleries is necessary in some areas to help such collaboration along.

Conservation surveying while carrying out protection and refurbishing programmes is very necessary. Such surveying information is essential both for obtaining facts and figures required for the administration and fund raising and for future grouping of problems to make the best use of conservators' time and to make effective economies in material acquisition and use. It is also needed to stimulate sensibly balanced research programmes, staff training, equipment utilization and so on. Conservation and historical survey records must all be linked in to a universally accepted computerized information system.

Trained personnel are now so scarce that close collaboration and exchange of specialists between institutions is desirable in the areas of conservation, prism camera photography and exhibition display.

Reference

1. Hartley, D., (1979). *The Land of England,* London, 5.

4.2

Bookbinding Leathers

4.2.1 The structure of leather

Betty M. Haines

Leathers suitable for the binding of books are prepared from the skins of cattle, calf, goat and pig. These skins have a similar basic structure consisting of protein fibres arranged in bundles which interweave in a three-dimensional manner. The structure is not homogeneous; the largest fibre bundles are to be found in the central region or the corium, but these subdivide and become finer as they approach the surface of the skin. The hairs are to be found in a distinct layer — the grain layer. Each species of animal has a distinctive skin structure which varies in thickness, dimension of constituent fibre bundle and proportion of total thickness occupied by the grain layer. The fibre weave is most compact over the back of the animal and least compact over the belly and axillae.

The strength of a leather is dependent not only on its total thickness but on the proportion of corium tissue present and the frequency with which the corium fibres interweave. In young animals the skin is thinner and fibre bundles smaller in dimension, but the ratio of grain layer to full thickness is the same as in more mature animals. Consequently a thinner leather retaining its full thickness is likely to be stronger than a thicker leather shaved down to the same substance.

The variation in skin structure found in different animal types permits the production of leather with widely different properties.

The comparison of leathers from different skins will indicate why some skins are stronger than others in relation to their thickness, and distinguish the different properties which are related to the different animals from which the skins are taken.

Skin structure

Leathers suitable for the binding of books are prepared from the skins of cattle, calf, goat, pig and to a lesser extent, sheep. All these skins have a similar basic structure consisting of innumerable bundles of protein fibres, the protein collagen. The collagen molecules are extremely long in relation to their cross-section and are naturally orientated during their formation into fibres and bundles of fibres *(Figure 4.1)*.

These fibre bundles interweave in a three-dimensional manner through the thickness of the skin, but the structure is not homogeneous. There are distinct layers in the skins as is shown by the cross-section of cattle hide in *Figure 4.2*. The fibre bundles vary in dimension at different levels within the skin. The largest are to be found in the central region or the corium, but these subdivide and become finer as they approach the surface of the skin.

Towards the inner or flesh surface which in life was adjacent to the muscle of the animal the fibres tend to run in a horizontal plane to form a limiting or flesh layer *(Figure 4.2)*. Towards the outer or grain surface, the fibre weave has to accommodate other structures such as hairs, which are found in one distinct layer, the grain layer *(Figures 4.2* and *4.3)*. This layer extends from the hair roots to the outer surface of the skin, which in the untreated raw skin is covered by the epidermis *(Figure 4.3)*.

The collagen fibres become increasingly fine as they pass through the grain layer. In the early stages of leather preparation the epidermis together with the hair is removed chemically, and then it is the

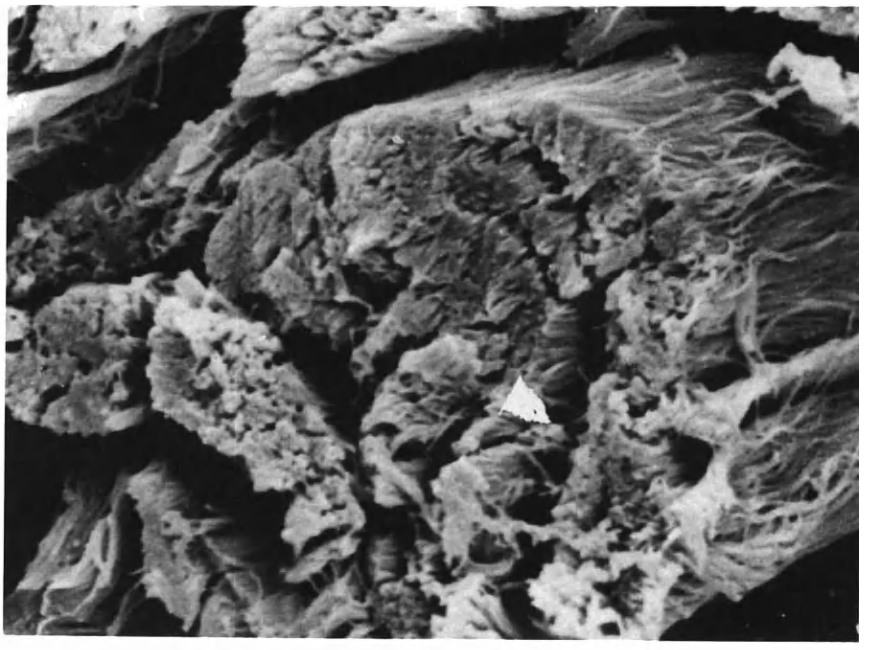


Figure 4.1.

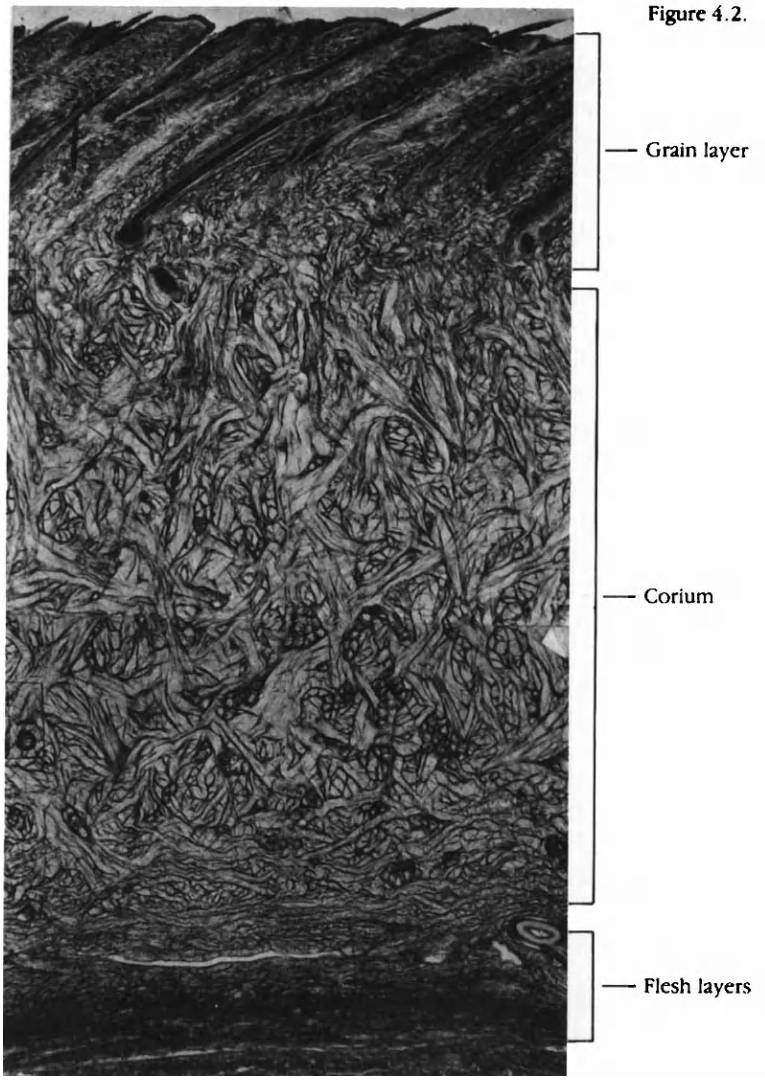


Figure 4.2.

compact interweaving of the fine collagen fibres which creates the smooth, aesthetically pleasing surface of the leather.

The fibrous weave and the variation in fibre size from corium to grain layer is best appreciated from a vertical section through a leather viewed under the scanning electron microscope *(Figures 4.4—4.6)*.

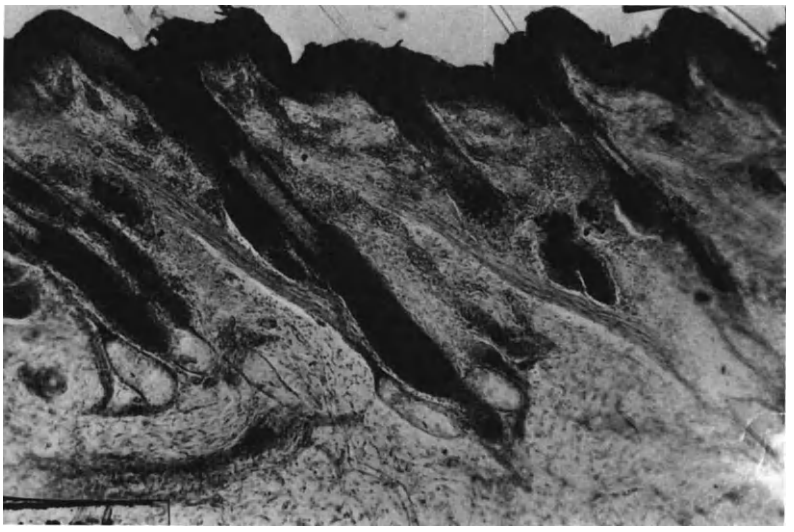


Figure 4.3.

Variation in structure between animal types

Each species of animal has a distinctive weave pattern: the skins vary in thickness, dimension of the constituent fibre bundles and in the proportion of the total thickness occupied by the grain layer, i.e. the layer in which the hairs are to be found. For example, the skins of mature cattle are generally 4-6 mm thick, the corium fibre bundles are relatively large and the grain layer occupies one sixth of the total thickness of the skin.

Such a skin is far too thick for use as an upholstery or a bookbinding leather unless it is split to give a layer that consists of the grain layer and part of the underlying corium *(Figure 4.7(a))*. The remainder of the corium forming the flesh split is used as a clothing or shoe suede *(Figure 4.7(b))*.

A calfskin is a miniature of the mature cattle skin *(Figure 4.8)*. The proportion of grain layer to corium is similar, but the total skin thickness and fibre bundle size are dependent on the age of the animal. Both increase with increasing age.

Sheepskins and goatskins range between 1 and 2 mm in thickness, the corium fibre bundles are relatively fine and the grain layer may occupy up to half the total thickness *(Figures 4.9—4.11)*.

There are several types of sheep, each type with a different skin structure. The hair sheep, indigenous in tropical countries, is a relatively small animal with a hair growth more like a goat. The skin is thin with a compact fibre weave as in goat *(Figures 4.9—4.11)*. The woolled sheep of European origin is a larger animal with dense wool growth; the skin is thicker and the corium fibre weave tends to be less compact than in goat or hair sheep *(Figure 4.11)*. Because of the high density of hairs (wool) in the grain layer, there is less interweaving of the fibres between corium and grain layer. Consequently there is often a looseness between these two layers. These features make this type of skin less suitable for a binding leather.

Pigskins differ from these other skins in that there is no distinct grain layer, the hair penetrating the full thickness of the skin *(Figure 4.12)*. Through the thickness of the skin the fibres interweave in a particularly compact manner and in a distinctive weave pattern.

Grain surface appearance

When in the leather making process the hairs are removed from the skin, the cavities left in the surface of the skin are arranged in a distinct pattern which is characteristic of each animal type. These surface patterns are shown in *Figures 4.13—4.18*.

Topographical differences in fibre weave

The natural fibre weave pattern of the skin not only varies through the thickness of the skin but varies according to its location on the original animal. The

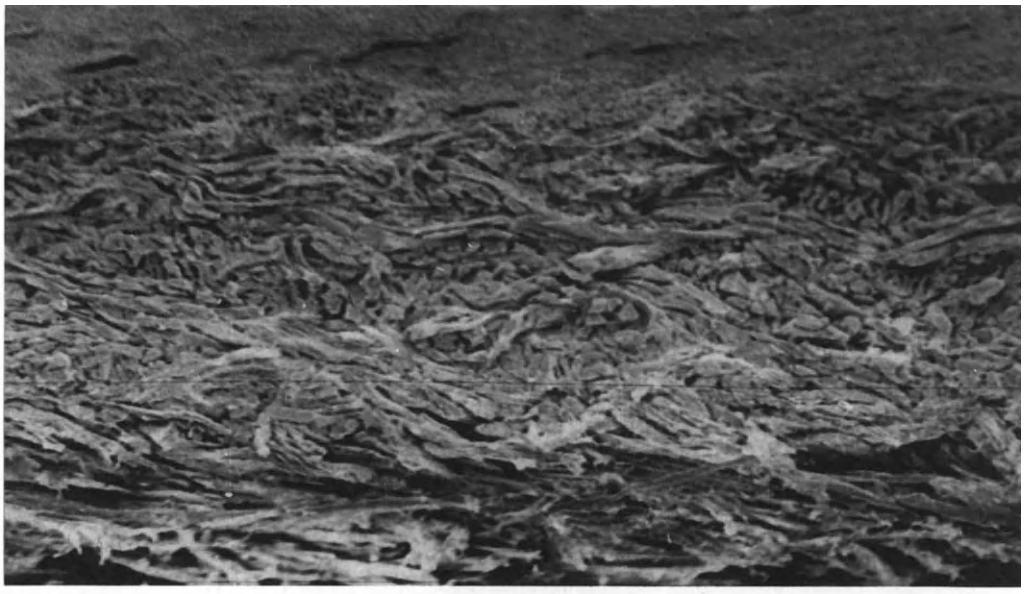
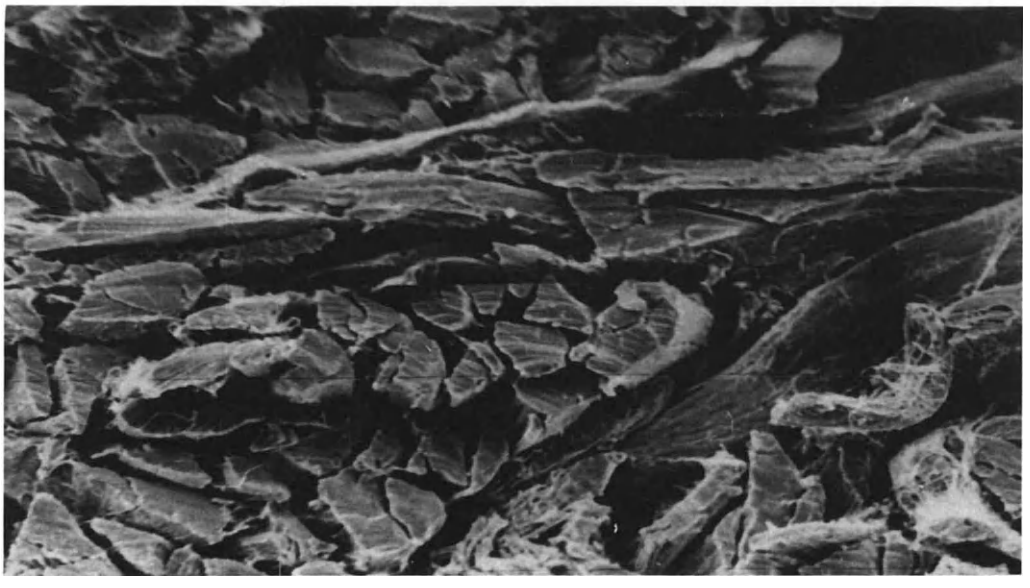


Figure 4.4.

Figure 4.5.



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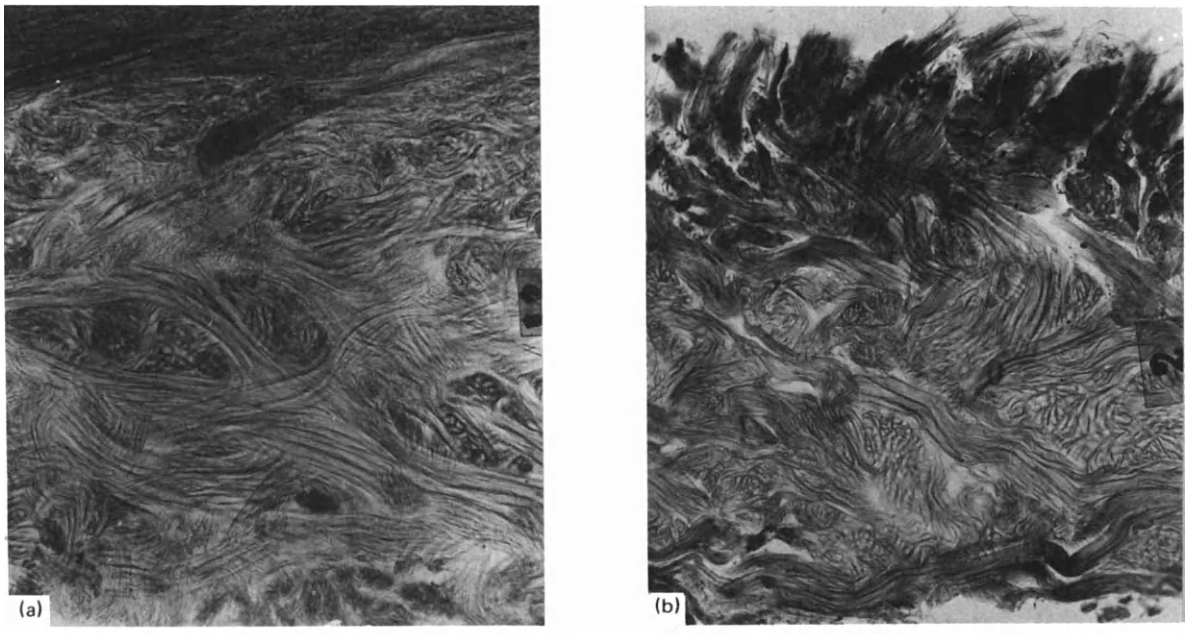


Figure 4.7.

Figure 4.8.

Figure 4.9.

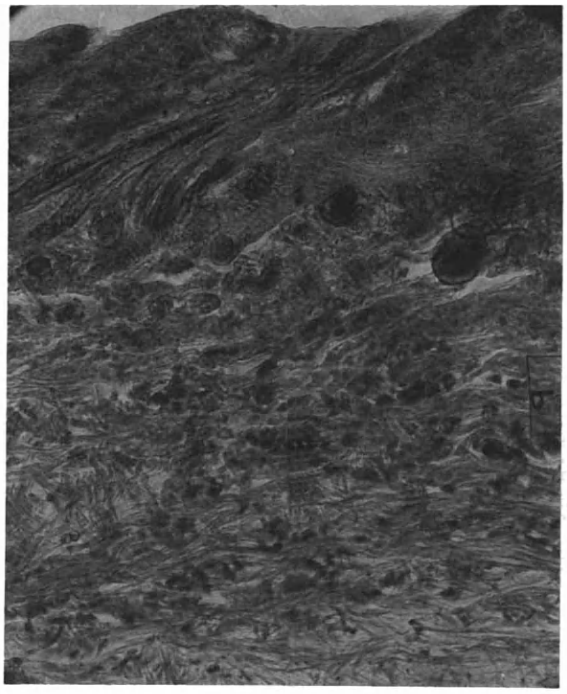


Figure 4.10.

Figure 4.11.

Figure 4.12.

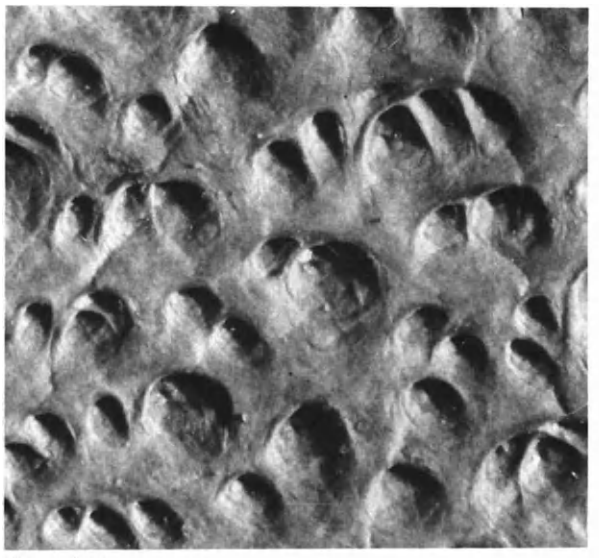


Figure 4.13.

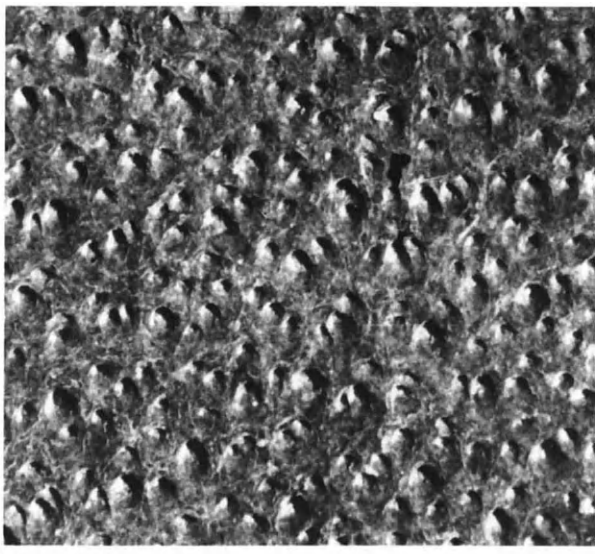


Figure 4.14.

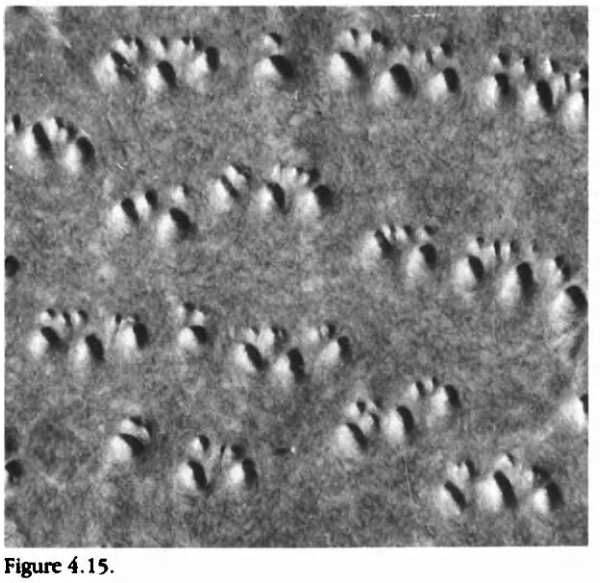


Figure 4.15.

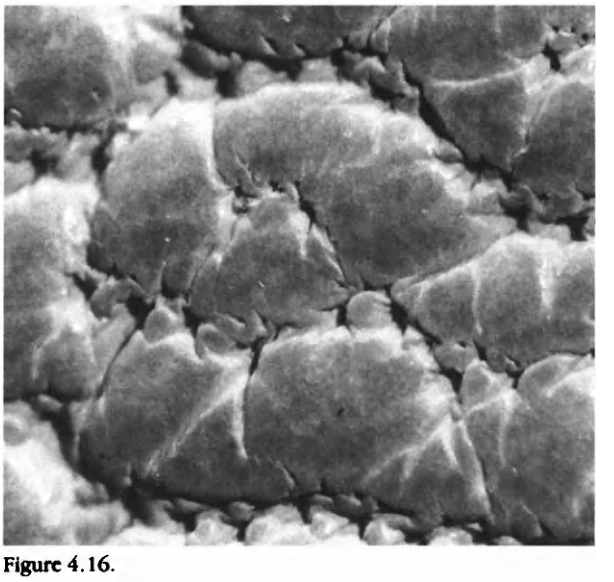


Figure 4.16.

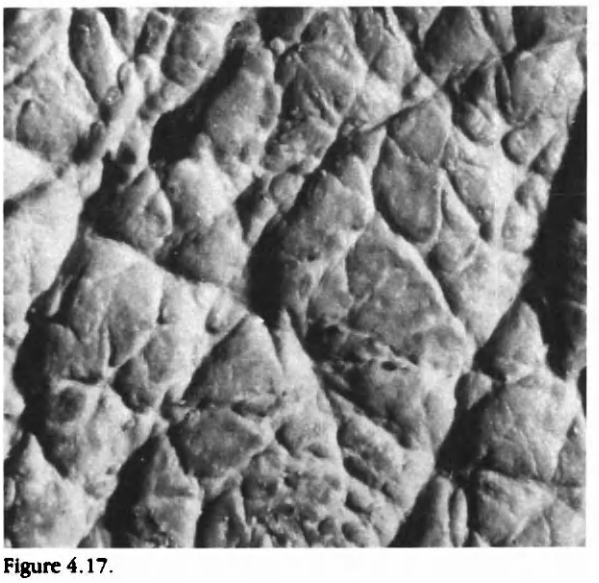


Figure 4.17.

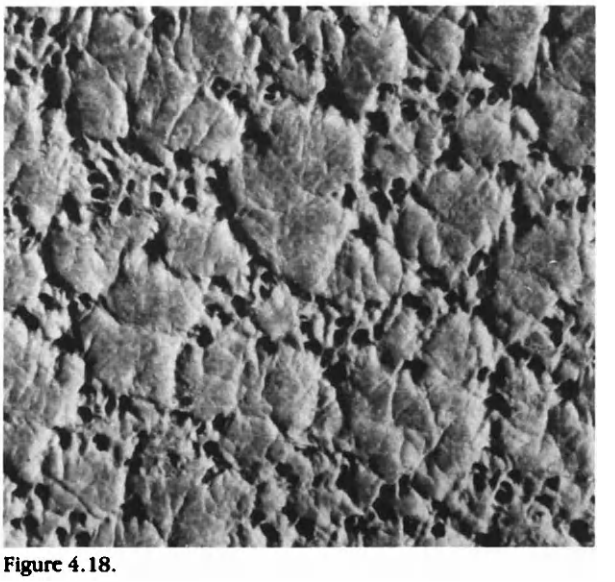


Figure 4.18.

skin which originally covered the back of the animal (A, *Figure 4.19)* has a more compact weave and a denser hair growth than that of the belly region (B, *Figure 4.19).* The least compact structure is to be found in the four axillae regions (C, *Figure 4.19).*

This variation in structure should be borne in mind when cutting skin for a binding. Any part of the binding that is likely to receive a greater degree of stress in use should not be cut from these looser regions, particularly the axillae. This difference in structure with location is shown in leathers from cattle hide and goatskin *(Figures 4.20* and *4.21).*

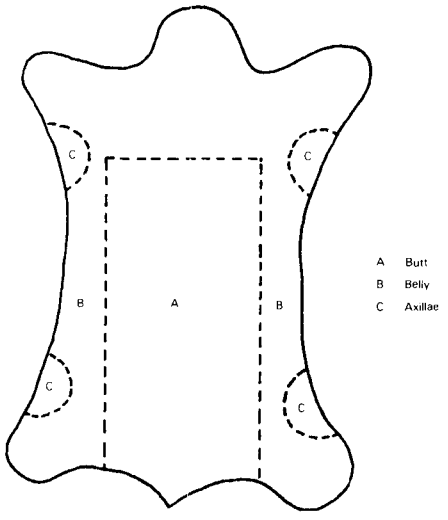


Figure 4.19. Regions within a skin: 6(A) Butt — the most compact region; (B) Belly — less compact region; (C) Axilla — least compact region.

Relation between fibre structure and strength

The strength of a leather is not only dependent on its total thickness but on the proportion that is corium tissue, and the frequency with which the corium fibres interweave. If a grain leather is made thinner by cutting away the corium tissues the reduction in strength will be disproportionally greater than the reduction in thickness. This is clearly demonstrated by *Figure 4.22.* The intact binding leather prepared from goatskin was 1.4 mm thick and tore at 7.5 kg *(Figure 4.22(a)).* In shaving this leather to 0.6 mm all the coarser fibre bundles of the corium were shaved away leaving only the grain layer *(Figure 4.22(b)).* This layer is relatively weak, and tore at 1.2 kg. The thickness had been reduced by half but the strength by five-sixths.

In young animals the skin is thinner and the constituent fibres smaller than in the more mature animal; *Figure 4.23* shows the structure of two grain leathers 1 mm in substance. One has been cut

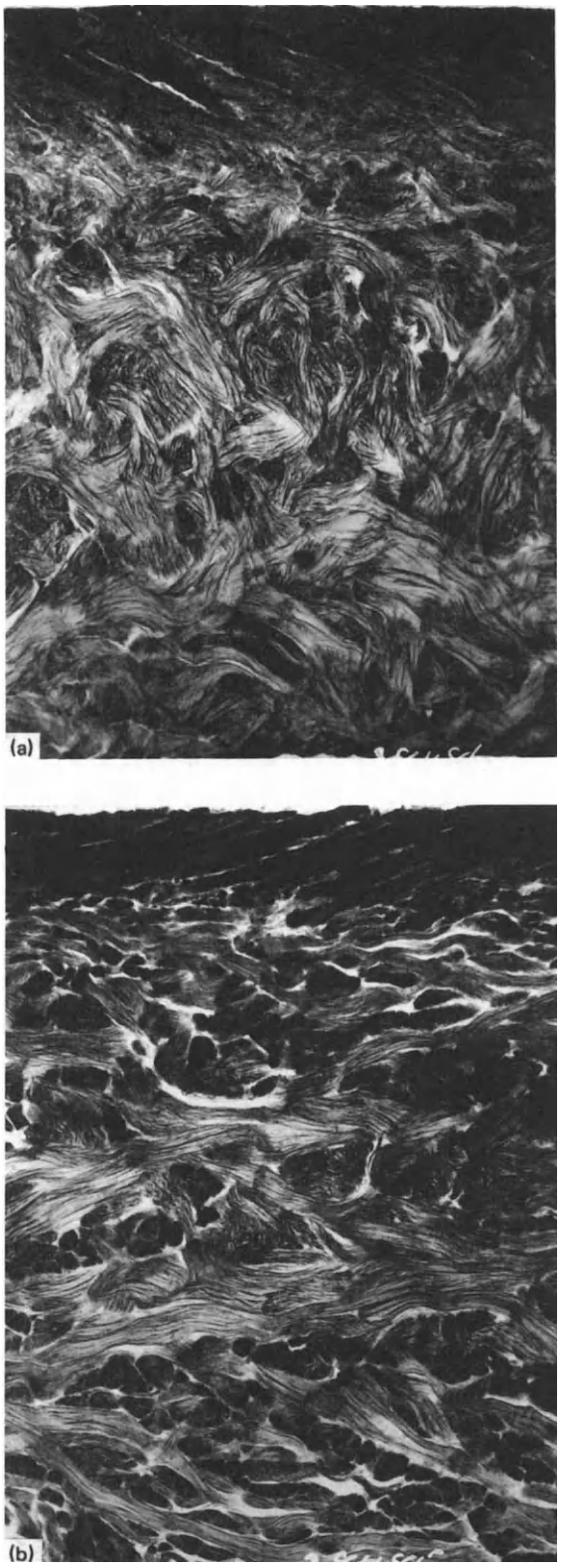
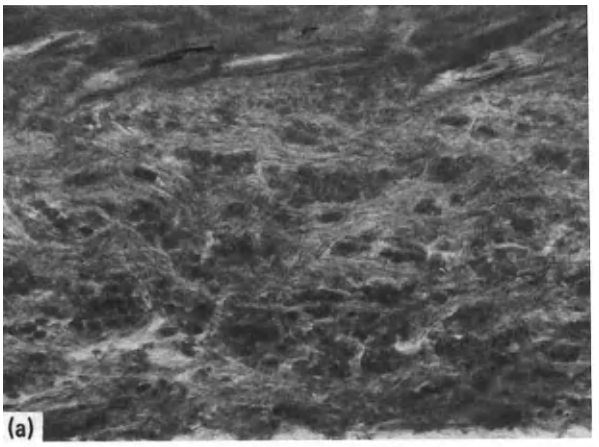


Figure 4.20.

from a mature cattle skin. The grain layer occupies two-thirds of the total thickness and there is insufficient depth of corium retained to permit frequent interweaving of the relatively large corium fibre bundles.



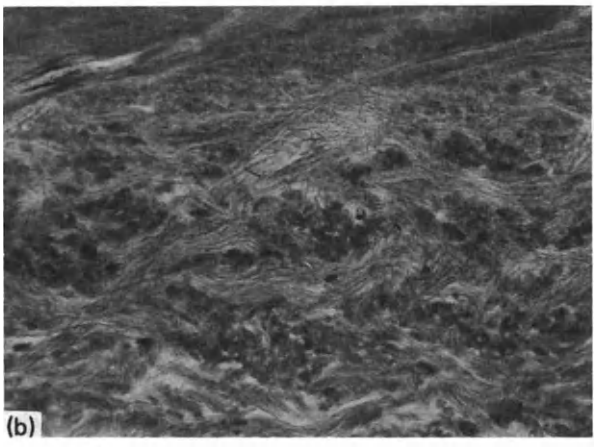


Figure 4.21.

Figure 4.22(a)

This leather tore at 2.5 kg. The other leather has been prepared from a calfskin and almost the full thickness of the skin has been retained. The grain layer occupies only one sixth of the total thickness and there is a frequent interweaving of the fine corium fibres. This leather tore at 6.8 kg.

The same principle that strength is dependent on the frequency with which the fibres interweave applies when cutting layers from the corium itself. For example, if thongs are cut from leather or skin the strength of the thong will depend on the frequency with which the fibre interweave with the cross-sectional face of the thong. A thong of 1 mm^2 cross-sectional face cut from the corium of a mature skin would be extremely weak, as there would be little interweaving of the coarse fibre bundles *(Figure 4.24(a))*. A thong cut from the corium of a calfskin would be considerably stronger *(Figure 4.24(b))*.

The reaction of the fibre weave to movement of leather

It is the fibrous weave that gives to leather its unique properties. The leather-making process can allow fine spaces to remain between the fibres so that they are free to move over each other within the fibre bundle and the bundle within the weave as a whole. This permits the leather to accommodate to stretching, compression or creasing imposed during the binding of a book or when the bound book is in use.

Figure 4.25 shows the way in which fibres at the grain surface move to accommodate to creasing of the grain surface.

When binding leather is tooled the pressure applied to the grain surface causes the underlying fibre weave to become more compact and the spaces between the fibre bundles and within the fibre bundles are reduced. The ability to retain this tooled shape depends on the degree of pressure applied and the tanning material used in the preparation of the leathers.

Vegetable tans fill the leather, that is excess tanning material fills the space between the fibres and this holds the fibres to shape when it is tooled or moulded *(Figure 4.26(a))*. Mineral tannages leave little excess tanning material between the fibres. The leathers have a lower relative density and tend to be springy failing to hold the impression of the tooling iron *(Figure 4.26(b))*.

The variation in skin structure found in different animal types provides the tanner with a wide range from which he can select the skin best suited for his type of leather. Although the tanner is then bound by the natural structure of the skin, his skill lies in

Figure 4.22(b).

Figure 4.23(a) and (b).

bringing about limited changes in the structure so as to produce leather of widely different properties.

The processes of leather production

Hides and skins removed from the carcase of an animal after slaughter receive five major treatments to convert them into leather:

(1) Curing or temporary stabilization of the flayed skin enables the skin to resist putrefaction during the storage or shipping period which usually occurs prior to the start of leather production proper.

(2) Depilation and fibre modification is the first stage of leather production and involves soaking, liming and unhairing, bating and pickling. This stage is essentially a purification of the leather-making protein, collagen, and its chemical and physical modification prior to tanning.

(3) Tanning or permanent stabilization of the purified leather-making protein makes the skin resistant to putrefaction and hydrothermal breakdown. Whereas raw skins putrefy when left in the wet state and shrink below 65°C when heated in water, tanned skins are resistant to putrefaction when left wet, and with the exception of oil and alum, tanned leathers shrink at temperatures above 75°C when heated in water.

(4) Post-tanning involves the preparation of the leather for dyeing and fat liquoring and the subsequent application of dyes for colouring and fats for giving softness, flexibility and stretch. The processes of preparation include neutralization of chrome-tanned leathers and retannage with a variety of organic and inorganic tanning materials. Post-tanning is completed by drying and the use of various mechanical operations which leave the leather with these characteristics predetermined by the process of liming, bating and fat liquoring.

(5) Finishing or surface coating is the application of film-forming materials (casein, nitrocellulose, polyacrylates, polyurethanes etc. which may or may not contain colouring materials such as dyes and pigments. Some leathers such as suede do not receive a film-forming surface coating. Other leathers receive a waxy finish which does not form a film.

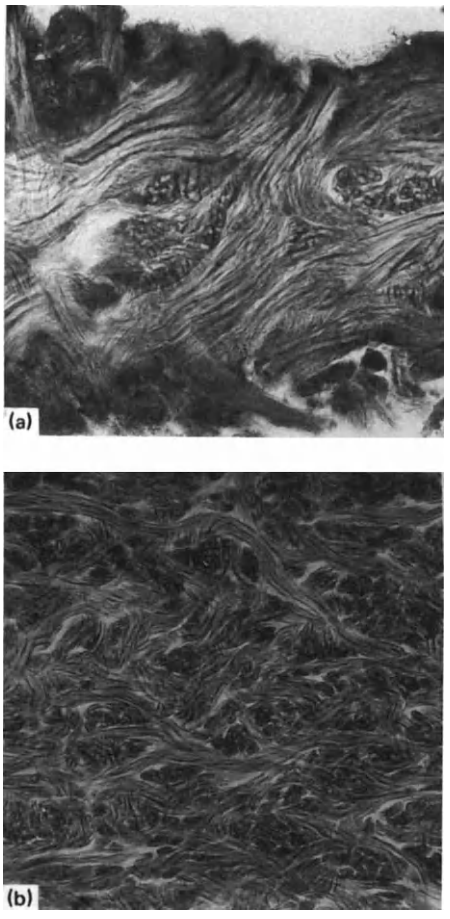


Figure 4.24.

Curing or temporary stabilization

Hides and skins are produced in many different parts of the world, and skins are often tanned at a great distance from their source of supply. In order to preserve the skins between their removal from the animal and the start of the leather-production process, the skins are cured. This can be done by drying or by the application of salt. It is very important that the curing process is quickly and easily reversible. If the skin is to be tanned soon after its removal from the carcase it can be cooled, frozen or treated with biocides which will preserve it for a few days. Some skins are exported in a partly processed state as pickled pelts or vegetable tanned crust or wet blue chrome leather.

Soaking, liming, unhairing, bating and pickling

On receiving a skin the tanner places it in water in order to reverse the curing process (drying or salting) to remove the salt and to wet the skin. This is achieved by immersion in water containing salts, surfactants, weak alkalis or enzymes. These materials help to disperse the interfibrilliary proteins and emulsify natural fats. This is the start of the process which eventually produces a purified collagen which can be converted into the permanent material known as leather.

The soaking process removes the soluble material that surrounds the fibres that make up skin and opens up the fibre structure so that the tanning and post tanning chemicals can penetrate into the skin. Soaking is easy where the skins have only been in the salted state for a month or so, and water at 25°C in a drum is sufficient. If the skin is dry then weak alkalis, salts and enzymes may be necessary to disperse the interfibre protein material. The degree to which this interfibre protein material is removed and the fibre structure opened up will affect the various finished leather properties such as softness, firmness, flexibility, etc.

When soaking is complete, strong alkalis such as lime and sodium hydroxide are used together with unhairing chemicals to remove the hair and to swell the skin. This process removes more of the

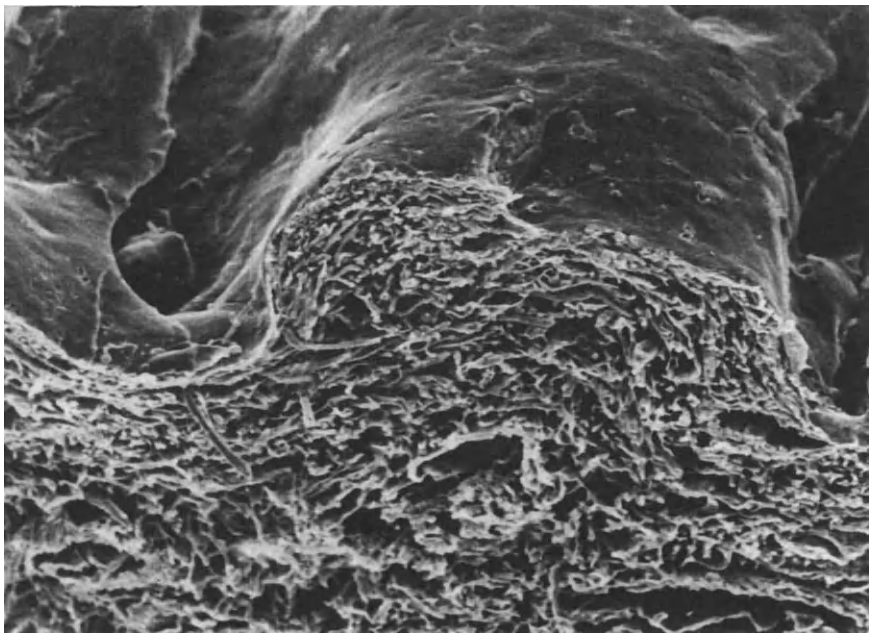


Figure 4.25.

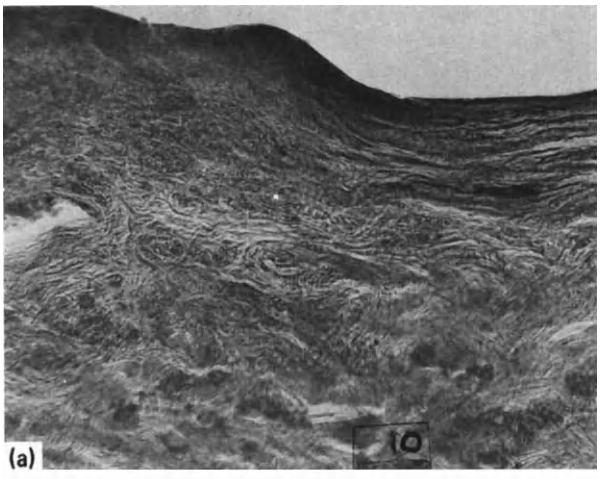


Figure 4.26.

interfibre protein and further opens up the fibre structure, making the fibres as fine as is required in the final leather. In sole leather this opening up and fibre splitting is kept to a minimum in order to achieve high abrasion resistance, whereas in gloving and bookbinding the fibres must be well split up to allow deep penetration of the fats which will give the leather the required softness, stretch or flexibility.

In earlier times, hair was taken off by hanging the skin up in a warm, humid atmosphere and allowing enzymes from a variety of micro-organisms to attack the hair roots and loosen the hair. This process was known as sweating, and was mainly used on woolskins because it yielded a long staple without danger of chemical attack on the wool. Today, sodium sulphide is used in large-scale leather production as a depilant. Sulphide attacks the keratin in hair causing it to dissolve. There are also some enzymes which can be used to achieve the same purpose. Having opened up the structure, the alkali must be removed in the process known as deliming. Weak acids and acid salts are used for this purpose and these leave the skin at a suitable pH for the bating process which follows. In bating, the delimed skin is treated with enzymes which remove collagen damaged in liming and also continue to solubize interfibre proteins. Pancreatic enzymes and enzymes produced from bacterial and mould cultures are used for bating. At one time dog dung and pigeon droppings were used for bating. Enzyme action gives a smoothness and silkiness to the grain of leather which is difficult to achieve any other way. After bating, the pH of the skin is 8-9 and must be lowered to between 2 and 5, according to

the type of tanning to be carried out. Skins to be tanned with inorganic tanning materials such as chromium, aluminium and zirconium are treated with acid and salt in a process known as pickling; this process lowers the pH to about 2. Skins to be tanned with vegetable tannins or aldellhydes are treated with weak organic acids or drenches to lower the pH to 4-5. The adjustment of pH prior to tanning is essential if the penetration and fixation of the tanning material is to be controlled.

Tanning

At this stage in the leathermaking process the skin has been purified by removing many of the non-leather-making materials from the skin. In addition, the fibres in the skin have been modified according to the type of leather being made. Ox hides intended for sole leather will have a noticeably different fibre structure appearance from hair sheepskin for gloving leather or wool sheepskin fleshes for chamois leathers. Skins will still rot if left for any period of time and the skin will shrink if treated with hot water. The shrinkage that occurs is irreversible because it involves damage to the protein collagen which now makes up 90-95% of the dry matter in the skin. In undamaged collagen the linear chains of amino acids making up the protein exist in an extended state; however, this extended state is only maintained by fairly weak chemical bonds called hydrogen bonds. When the skin is heated, the relatively weak hydrogen bonds are broken or disrupted and the chains of amino acids coil up and lose their extended linear form. This change at a molecular level in the protein shows itself as shrinkage in the skin. If the skin is kept at a high temperature for a long time the collagen dissolves and becomes gelatin.

The process of tanning gives permanence to the skin by introducing cross-links between chains of amino-acids, like rungs in a ladder or ties in a brick wall. Some of the cross-links are fairly weak, as in the case of vegetable tannins, and the leather produced will shrink at 75-85°C. Other cross-links such as those involving chromium and aldehydes are more stable. Chromium-tanned leathers may withstand boiling and aldehydes are resistant to the action of a wide variety of chemicals and perspiration. Leathers tanned with aluminium or oil will still shrink at the same temperature as raw skin.

Tanning materials can be divided into two main groups:

Inorganic:	Aluminium (white) Chromium (blue-green) Zirconium (white)
Organic:	Natural products (vegetable tannins; cod oil)
Synthetic:	(formaldehyde, glutaraldehyde, synthetic tannins, resin tannins, dialdehyde starch)

Vegetable tannins are extracted from plant materials and can be divided into two broad chemical groups described as hydrolysable and condensed tannins. Examples of vegetable tannins and their sources are given below:

Bark:	*†wattle; *oak; *†chestnut; *mangrove; hemlock
Wood:	*†quebracho; *oak; *†chestnut
Fruit:	†myrabolams; †valonia; divi-divi; algarobilla, tara; sant; pomegranate
Leaves:	†sumach; †gambier
Root:	canaigre
Growths:	turkish galls; chinese galls

*Condensed tannins

†Major vegetable tannins used in Northern Hemisphere

The colour of vegetable-tanned leather varies from pale biscuit (sumach) to dark brown (mangrove) and the shrinkage temperature ranges from 70-75°C (hydrolysables) up to 85-90°C (condensed).

All tanning materials have their own properties and are carefully chosen according to the type of leather being made.

Neutralization, retanning, dyeing and fat liquoring

After tanning, some leathers are acid (chromium) and must be neutralized before being retanned, dyed and fat liquored. Neutralization is achieved by using weak alkalis (borax; sodium bicarbonate) or weak acid salts (sodium acetate; calcium formate). After neutralization the leather may be retanned to give it the required feel, to fill empty spaces in the fibre structure or to prepare it for dyeing. In earlier times, dyewoods were used for colouring leather. Today, leather is coloured with synthetic dyestuffs and the whole range of dyestuffs including acid, basic, direct, vat, sulphur and reactive dyes are used on leather. The choice of dyestuff will depend on the properties required in the finished leathers; these will include lightfastness, washfastness, resistance to perspiration, ability to be dry cleaned, brightness of colour and depth of shade. The final wet process involves the introduction of fats into the leather. Some leathers such as sole leather or waterproof leathers for walking boots may be

treated with raw fats based on tallow, lard and fish oils. Such materials are rubbed onto damp leather and penetrate slowly as the leather dries. However, most fats are introduced in the form of an oil-in-water emulsion and they have to be chemically modified by treatment with sulphuric acid or sodium sulphite. A wide variety of plant, animal and synthetic oils are used in leather production: these include cod, neatsfoot, castor, coconut and synthetic sperm oil substitutes. As in the case of dyes, the fat liquor is chosen carefully according to the type of leather being made.

In the modern leather industry the processes of retanning, dyeing and fat liquoring are frequently carried out at the same time.

Some leathers may require to be made waterproof or resistant to dirt. Treatments based on the use of silicones, fluorocarbons, alkenyl succinic acids, long-chain dicarboxylic acids and chrome stearato chlorides are applied at this point or after drying as is appropriate to the waterproofing agent chosen.

Drying and mechanical treatments

After the final wet process the leather is drained and then dried. The leather may be dried by hanging, toggling on frames or nailing on boards, paste dried sticking onto glass plates or vacuum dried. Each type of leather is dried in its particular way. Sole leather which is sold by weight is dried by hanging, corrected grain upper leathers for shoes is sold by area and must be smooth and flat for finishing and so is dried by paste drying.

Following drying, the leather may be subjected to mechanical treatments. Two treatments are discussed below:

Staking: the dried, humidified leather containing about 25% moisture is kneaded, pulled and flexed to separate the fibres and to soften the leather.

Buffing: leathers which are to be pigment finished may be treated with a fine emery paper to lightly abraid the grain surface to provide a key for fixing the finish. The effect is similar to rubbing down paintwork prior to applying the paint. Suede leathers are buffed on the flesh side to produce the nap (velvetlike fibre layer) which is characteristic of this type of leather.

Finishing

In this, the final process of leather production, the leather is treated by spraying or padding-on a preparation of pigments dispersed in a film-forming resin emulsion. As in house painting, a series of coats are applied, starting with a base coat and followed by a number of middle and top coats. It is important that the base coat has good adhesion to the leather and that the firmness and flexibility of the resin (polymer) film matches that of the leather. A hard inflexible polymer on a soft flexible leather will crack when the leather is flexed and this will allow materials from the atmosphere to be absorbed through the protective surface. Top coats are carefully chosen to give easy clean finish properties, water or solvent resistance and good scuff resistance. A pigmented finish is usually applied when the grain of the leather is seen to be damaged by the effects of disease, pests or mechanical defects such as barbed-wire scratches. However, many skins have a perfect grain and this natural grain is retained and shown off to perfection by using non-pigmented finishes.

The tanner has a huge range of finishing materials and techniques at his disposal, and by careful selection of these he is able to produce a bewildering array of finishes. Finishes may be dull or sparkling, shiny or matt, smooth and cold or full and warm, slippery or waxy. Special effects may be produced by embossing artificial patterns on the surface, two-tone spraying or screen printing. The tanner can produce leathers which are at the same time both functional and aesthetically pleasing — a pleasure to work with and a joy to behold.

4.2.2. The manufacture of bookbinding leathers

Peter G. Ellement and *David H. Tuck*

In the manufacture of bookbinding leathers the tanner has to take into account the properties which will be required in the finished leather — substance, handle and feel, durability, flexural endurance, finish. By the careful selection of raw skins, the correct choice of processing conditions and the use of modern chemical preparations the tanner can produce a leather which is not only pleasing to look at and to handle but which has improved resistance to mechanical damage and to the ravages of atmospheric pollution.

The process conditions for the production of a variety of bookbinding leathers (calfskin, goatskin, sheepskin and pigskin) are discussed and advice is given on the care and maintenance of books bound in leather.

Bookbinding leather manufacture

In the manufacture of bookbinding leathers the tanner has to take into account the following properties which will be required in the finished leather:

Substance or thickness

For most purposes a leather of between 0.5 and 0.6 mm is required and only in the case of heavy ledgers and similar heavy bindings is a leather of 0.8 and 1.00 mm needed.

Ideally, skins or leathers for a particular thickness of finished leather should be selected in the raw or crust (semi-tanned) state to avoid the need to remove excessive amounts of leather by shaving (paring) which can result in low tear strength. Unfortunately, the traditional vegetable-tanning methods used for bookbinding leathers tend to increase the thickness of the grain layer, so that in the final finished leather the grain occupies a large percentage of the total leather thickness. This effect can be reduced by using tannages based on chromium III sulphate and by a variety of processing techniques designed to keep the thickness of the grain to a minimum. Strength and durability may be enhanced by the use of chromium salts but this may be at the expense of the handle of the leather and its ability to be tooled.

Handle and feel

It must always be a pleasure to hold a leather-bound book and part of that pleasure comes from the feel and handle of the leather. Traditional tannages based on vegetable tannins and aluminium salts fill the interfibre spaces of the leather giving a round, full feel and handle. The use of chromium salts produces thinner flatter leathers which may require fairly large amounts of fats to give them the required handle, though flexibility may be achieved with quite small amounts of fat. The presence of chromium makes wetting and tooling more difficult but against this must be set the positive advantages of improved durability, better tear strength and a wider range of brightly dyed leathers with improved colour fastness to light, water and perspiration.

A compromise position is frequently achieved by producing chromium retanned (chromium tannage followed by vegetable tannage) and semi-chrome tanned (vegetable tannage followed by chromium tannage) leathers having a low chromium content (0.5-10% Cr_2O_3 w/w).

Durability

The long-term resistance of leather to the effects of atmospheric contamination (chemicals, radiation, moisture, heat) and handling (perspiration, grease and dirt) is a major requirement of bookbinding leathers. The tanner has available to him an increasing variety of chemicals developed for today's consumer-orientated society and he is able to make a choice when it comes to controlling such factors as lightfastness and the resistance to water, solvents and perspiration. Also, he is restricted in the use of many materials, particularly surface coatings, by the requirements of the finished leather (wettability, compatability with adhesives, surface appearance, etc.). However, he cannot predict the effect of many of these new chemical products on the long-term durability of leather and can only make a choice within the broad guidelines of (1) avoiding highly unsaturated organic compounds, (2) restricting the use of products likely to produce strong acids by oxidation, chemical degradation, etc., and (3) controlling the pH.

Flexural endurance

This requirement is met by the careful selection of skins and the control of the leather making processes to give leathers with a close compact fibre structure in which the degree of fibre splitting allows the fibres to move independently of each other. The lubrication of the fibre structure with a suitable fatty material is important in producing a leather which is flexible but not soft.

Finish (surface coating)

The final stage of leather production is the application of the finish or surface treatment. The finish has a number of important roles. Aesthetically, the finish gives the leather the required appearance (colour, gloss, matt) and texture (rough, smooth, warm, waxy). Functionally, the finish provides protection against both chemical and physical damage and will affect the extent to which dirt is taken up by the leather. The finish must flex with the leather without cracking but at the same time should allow the penetration of lubricants and protective chemicals (fungicides, buffer salts) used in proprietary leather dressings.

Suitable finishes for bookbinding leathers are based on protein materials (casein, albumen) and synthetic poly amides. These materials enable the leather to be friction glazed which highlights the unique grain characteristics of the leather as well as giving a base to which gold blocking has good adhesion. The properties of the finish are very dependent on the wettability of the leather surface. Water-based protein finishes have poor resistance to wet rubbing and are fixed by cross-linking with formaldehyde. Fixing hardens the finish film and reduces its flexibility, so a plasticizer in the form of a wax or mucilage is incorporated in the finish to counter this effect. Such materials also help to fill the grain of the leather and to protect it while in use. Modern film-forming agents based on acrylates give excellent finish properties but cannot be used where the leather is to be gold blocked. If the grain of the leather is damaged or of uneven appearance then pigments can be incorporated in the finish and used to hide the damage.

Suitable skins for bookbinding leathers include calfskin, goatskin, pigskin and coarse wool and hair sheepskin, but skins from other animal species and bovine hides may also be used. In the following sections tanning processes for four types of skins are considered.

Calfskin bookbinding leathers

There are three main types of bookbinding leathers made from calfskins:

(1) Coloured or smooth calf.
(2) Fair calf (undyed and finished on the grain).
(3) Rough calf (fleshside suede finish).

The rawstock selected for this type of leather is from young calfskin having an area of 7 to 9ft.^{2} Thin skins are preferred if good tear strength is to be achieved. The skins are received in the salted condition and are initially soaked in water to rehydrate the fibres, remove the salt and solubilize globular proteins held between the collogen fibres. This latter effect is continued in the liming process where the addition of sodium sulphide removes the hair and the high alkalinity causes osmotic swelling and splitting of the fibres. These changes are essential if the correct degree of flexibility is to be obtained in the final leather. A typical soaking and liming procedure would be as follows. (The percentages are all of the wet salted weight.)

(A) Soaking: 18-24 hours in a pit or paddle with several changes of water.

(B) Liming: First paddle 500% water at 20°C.
5% hydrated lime — $Ca(OH)_2$.
2% sodium sulphide — Na_2S (60% purity).
Paddle 5 minutes per hour for 4 days and remove the hair by hand or machine.

Second paddle 500% water at 20°C.
5% hydrated lime.

The skins are paddled intermittently for a further three or four days and fleshed to remove adhering adipose tissue from the flesh side. The skins are then washed and reacted with weak acids to neutralize the alkalinity. Finally they are treated with enzymes to further soften them and washed in cold water to prepare them for tanning.

Up to the beginning of this century calfskins for bookbinding were either tanned with the tanning obtained from oak bark or from sumach leaf. In the former case the skins were laid flat for several months in pits containing a weak infusion of oak bark tannin. The skins were pulled up from the pits and replaced every few days until they were evenly tanned through. After washing to remove surface tannin the tanned leathers were oiled with a vegetable oil and hung to dry. In the dry condition they were described as 'bark-tanned calfskins' and were stored in this crust condition until required for dressing. The skins to be sumach tanned were first sewn up along the edges of the skin until only a small opening remained in one hind shank. An infusion of sumach tanning was poured in and the opening finally sewn up. The skins now inflated with sumach infusion were floated in large vats of sumach tannin, where they remained for several weeks until fully tanned. The skins were then opened up, washed, oiled and dried. In this dry crust state the leathers were known as 'bag or bottle-tanned sumach calf' and were considered as the best binding leathers then available.

Sumach gave a very pale leather with excellent lightfastness and good dyeing properties. The presence of weak acid salts ensures good protection against atmospheric deterioration.

These older tanning methods were time consuming and labour intensive and have now been replaced by more economic methods based on paddle and drum tannages using other tanning materials such as blends of myrabolams and mimosa. These tannages take only seven to ten days and yield creamy off white-coloured leathers. These leathers are not so durable as the older leathers and slowly turn pink or red on ageing. Improved durability can be obtained by a light chromium tannage prior to the vegetable tannage.

From the dry crusted state the leathers are wet back (rehydrated) and carefully shaved to the required thickness. Proper selection should ensure that a minimum of shaving is required.

The preparation of the leather for dyeing includes stripping with alkali (sodium bicarbonate, borax) to remove surface tans, bleaching to brighten the colour and a retannage with sumach to retan the grain and give level dyeing properties. Modern leathers may be retanned with chromium to give improved durability and good dyeing properties. The leathers are then dyed with acid dyes of good lightfastness, the dyestuffs being added slowly to obtain good levelness. In the case of fair calf dyeing is omitted.

Finally, the leather is treated in a drum with an emulsion of sulphated vegetable oil of low unsaturation which acts as a lubricant and protects the dry leather in use. The leather is then set out flat and stretched out by nailing or toggling and allowed to dry. Where applicable (not chromium tanned leathers) protective salts may be added by drumming, dipping or spraying.

The finishing operation begins with a light staking which flexes and separates the fibres and softens the skin; this may be followed by a light buffing on the flesh side to remove any loose tissue and to give a clean tidy appearance.

The coloured calf are then sprayed with a plain non-pigmented finish to provide a protective film and gloss to the grain. A typical formulation is:

200 parts casein (15% solids w/v).
100 parts wax emulsion (15% solids w/v).
700 parts water.
5-10 parts aniline dyestuff if required.

When dry, the leather is sprayed with a 10% solution of formalin available as a 40% w/w formaldehyde solution to fix the finish. After drying again, the leather is either ironed on a rotary press or kiss plated on a hydraulic press.

Fair calf which are not dyed are simply dusted with french chalk and ironed or plated.

Rough calf are carefully buffed on the flesh side to produce a fine even nap or suede surface.

Goatskin bookbinding leathers

There is a great variety of bookbinding leather made from goatskin and this includes the following types:

(1) Oasis goatskin leather (Niger goat) made from vegetable-tanned goatskin produced in Nigeria. The leather surface has a drawn grain appearance.
(2) Morocco leathers produced from sumach-tanned goatskins:
    (a) Levant-grain moroccos have a bold shrunken grain.
    (b) Semi-Levant grain moroccos have a fine shrunken grain.
    (c) Long-grain moroccos in which the grain pattern produced by boarding runs vertically down the skin from neck to tail.
    (d) Willow-grain moroccos in which the grain pattern produced by boarding runs horizontally across the skin from flank to flank.
    (e) Cross-grain moroccos in which the grain pattern produced by boarding runs diagonally across the skin.
(3) Imitation moroccos made from goatskin tanned with vegetable tans other than sumach. Skins embossed with a morocco grain and then boarded are called assisted morocco.

An example of imitation morocco is hard grain goatskin made from EI tanned goatskin boarded in eight directions both wet and dry.

Goatskins possess a well-developed densely woven fibre structure which yields thin hard-wearing leather. They have a bold grain pattern which can be accentuated by glazing and boarding.

Goatskin leathers are processed to the dyed fat liquored condition in the conventional manner as described above.

In the case of oasis goat and levant moroccos fermented or lightly acidified tanning solutions are used. The acid causes the skin to swell and shrink in area during the early stages of tanning, thus creating an attractive distortion of the grain surface which is preserved during the subsequent tanning and dressing processes.

Finishes are generally protein based and involve a casein base coat followed by middle and top coat finishes made from mixtures of casein and albumen fixed with formaldehyde. Where a leather is to be boarded wet to produce a pronounced raised grain, as in hard-grained moroccos, then nitro cellulose finishes are preferred because they possess greater resistance to water. In addition they produce a sparkling finish on the leather.

Boarding followed by glazing gives the typical two-tone colour pattern associated with grained goatskin leathers.

Sheepskin bookbinding leathers

There are two main groups of bookbinding leathers made from sheepskins:

(1) Roans.
(2) Basils.

The first group of leathers are of better quality because they are made from the skins of coarse-woolled sheep.

These skins possess a more well-developed and compact fibre structure than the wool sheepskin from which basils are produced. The latter tend to have a loose fibre weave which adversely affects the properties of the leather. They are less expensive than roans and play an important role at the cheaper end of the binding market.

Sheepskin bookbinding leathers are produced by the normal leather-production techniques used to tan calf and goat but where long-term durability is not required short float and dry-drum tannages may be used on pickled (sodium chloride and sulphuric acid) sheepskin. Such processes give very pale uniform leathers but lightfastness properties may be impaired as condensed tannins of the mimosa type are usually used for this type of processing.

In addition to the full-substance leathers produced from roans and basils the grain splits of sheepskin are used to manufacture skiver bookbinding leathers. These leathers are produced by splitting the full-substance sheepskin after liming or immediately before tanning. These leathers are extremely thin, ranging from flywing (0.2 mm) to heavyweight (0.4-0.5 mm) and are available in a wide variety of glazed, printed and smooth finishes. They are frequently strengthened by an application of alginate mucilage to the flesh side, when they are known as moss backed skivers.

Pigskin bookbinding leathers

For many centuries pigskins have been used for the manufacture of alum tanned (or tawed) bookbinding leathers which have always been in demand because of their superb appearance and handle and their high resistance to deterioration. The main disadvantage is that the tannage is reversible and the aluminium salts easily removed by washing with water. More stable leathers can be produced by the combined use of vegetable tannins or poly hydroxy phenols and aluminium salts. The colour may be impaired but the durability is improved.

A typical modern procedure in drums for producing this leather is given below:

(A) Raw material: Wet salted pigskin arising from pork production.

(B) Soaking: Weigh salted skins.
300% water at 25°C.
0.5% sodium carbonate.
0.25% non-ionic detergent.
Drum intermittently for 2 hours, drain off the liquor and repeat the process over 18 hours.

(C) Green flesh to mechanically remove fat and fleshy tissues from the flesh side.

(D) Debristling: 100% water at 25°C.
10% sodium sulphide (60% w/w).
Drum 30 minutes and wash well.

(E) Liming: 200% water at 25°C.
5% hydrated lime.
2% sodium sulphide (60% w/w).
Drum intermittently for three to four days and wash with cold water.

(F) Lime flesh to remove any adhering tissue and split the limed pelt to give a grain split 2.0 mm thick.

(G) Second liming: 200% water at 25°C.
5% hydrated lime.
Intermittent drumming for three days.

The processes B-G are designed to clean the skin, to remove unwanted protein material and to modify the fibre structure to allow tanning materials and fats to penetrate. The long alkaline treatment also helps to disperse the grease present in the skins. After the second liming the skins are weighed and well washed.

(H) Deliming and bating: 200% water at 35°C.
2% ammonium chloride.
Drum for 30 minutes and add 0.75% strong pancreatic bate (enzyme). Drum for 3 hours.

(I) Degreasing: 300% water at 30°C.
5% trichlorethylene.
3% non-ionic detergent.
Drum for one hour and wash well.

Processes (H) and (I) continue the removal of unwanted proteins and grease and bating helps to soften and relax the skin.

(J) Tanning: 100% water at 25°C.
5% sodium chloride.
10% aluminium sulphate.
1% electrolyte stable fast to light oil emulsion.
Drum intermittently for 24 hours and slowly raise the pH to an equilibrium value of 4.5 with sodium acetate. Drum intermittently for a further 24 hours and pile the skins for 48 hours.

Samm the skins to remove excess water and shave to give a thickness of 0.7 mm.

(K) Retanning and fat liquoring: 100% water at 40°C.
10% basic aluminium chloride.
8% electrolyte stable, fast to light oil emulsion.
5% white talc powder or French chalk.
Drum for four hours and pile for 24 hours.

(L) Drying: The wet leather is sammed to remove excess water, set out to flatten it and to remove creases and dried by stretching out on frames.

(M) Finishing: The dried leather is staked to soften it, buffed on the flesh side to give a clean even surface and finally the grain is lightly dusted with French chalk.

The care and maintenance of books bound in leather

Much has been said but, apart from the publications of Banks, Horton, Plenderleith and the Library of Congress, the literature on the subject is restricted. Most conservators have their own preferred formulations and preparations for the cleaning and after-care of leather though many of these have become standardized in the form of the British Museum Leather Dressing.

In the matter of the care of leather it is important to keep treatments and formulations as simple as possible and to avoid putting into the leather substances whose long-term effects are unknown.

In general there is very little that can be added to the advice and procedures suggested by Waterer. However, there is much useful information that can be found in older books on shoe dressings, shoe room techniques and leather finishing. They contain useful advice on the care of wax, protein and cellulose finishes which were used on shoe

leathers of the time and are still widely used on bookbinding leathers today. Trade literature from chemical companies' manufacturing finishes for leather should provide museum staff with a valuable insight into the methods and composition of finishes used on modern leathers. It is important that the type of leather and the nature of the finish should be determined before cleaning begins. The following comments relate to grain finished leathers only and not to suedes.

(1) Regular care: dust should be removed with a soft duster and finger marks removed with a soft rubber eraser or plastic foam sponge. The leather should be polished using a carnauba wax (hard film) or beeswax (waxy film) preparation.

(2) Occasional care:

(a) Cleaning: remove dust and wipe over with a cloth dampened with white spirit or with a barely damp sponge and a little good soap. Remove surface soap and dry.

(b) Protection from acidity: (vegetable-tanned leathers only) sponge with a 5% solution of potassium lactate containing a fungicide.
Leathers already containing acid may be pretreated by sponging with 1% w/v solution of borax. Dry thoroughly.

(c) Lubrication and polishing.

Common leather dressings contain the following components:

(A) A lubricant (lanolin, neatsfoot oil) which is required to penetrate rapidly and to cover the fibre surfaces in a thin film to allow ease of movement of fibres. Raw oils have excellent lubricating properties but as they are not fixed in the leather they can migrate during use and give rise to greasy surfaces if too much is applied. The lubricant may also have a plasticizing effect on the finish film, ensuring that it remains flexible.

(B) A film-forming material (carnauba wax, beeswax) which is capable of being polished. The wax may also plasticize the finished film and protect the surface against dirt. The wax film is easily removed together with the dirt by a cloth dampened with white spirit. In addition, the careful choice of wax emulsion can alter the surface feel (hard, waxy, etc.).

(C) An antiseptic against mould (cedar wood oil, orthophenyl phenol).

(D) A diluting medium (hexane, 1.1.1 trichlorethane) which rapidly pentrates and acts as a carrier for the lower molecular weight lubricant. It should be fairly volatile so that the treated surface 'dries' quickly.

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At the time of going to press B. M. Haines of the British Leather Manufacturers' Research Association had just presented extensive new recommendations commissioned by the Conservation Department of the British Library which are being evaluated by the conservation community.

Discussion Notes

The components of a leather dressing

Lubricant

A lubricant is required to lubricate the fibre structure and reduce internal friction. It is essential that it should be non-reactive. Oils which have the capacity of being oxidized will turn yellow, and oils which have been treated chemically to make them emulsifiable in water (such as sulphated, sulphited and sulphenated oils) are likely to decompose over a period of time. In the case of sulphated oils, the attached emulsifying agents will eventually turn up as sulphuric acid. This is why there is a move towards using natural oils, which have other hydrophilic properties, and non-ionic emulsified oils. It is very important that the oil which is used has long-term stability and does not have the capacity to break down or form harmful products within the leather over a long period of time.

Wax or grease

This has two functions. The first is to form a film, to exclude oxygen and other gaseous pollutants, and to give a protective coating to the leather to protect it from water, etc. This type of damage can easily be seen in shelved books, where the exposed spine is rotted, but where the sides, compressed between other volumes, remains comparatively undamaged. A leather dressing therefore needs something which is capable of forming a film and excluding air. A wax will also give the book a pleasant and attractive feel. The second function of wax or grease in a dressing is to control the viscosity of the mixture. An oil applied entirely by itself will penetrate very quickly and may collect in excessive amounts in the looser parts of the skin and result in darkened areas. Wax will give a semi-crystalline structure to the oil/wax mixture, and will increase the light reflectance of the dressing. You will not get the same degree of darkening that you do from oil by itself.

Carrying medium

This is generally a solvent of some kind, generally an inert one such as hexane or white spirit. Alcohol/water mixtures can also be used. These are for carrying the dressing into the leather.

(D. H. Tuck)

Refurbishing and leather finishes

The finishes applied to some late nineteenth and twentieth-century leathers need to be examined, as does the importance of rehydrating leathers before refurbishing them. There are also problems in applying an all-purpose leather dressing, with its tendency to carry right through degraded leathers. Experiments have been carried out using a staged procedure, in which rotted leathers are first treated with a size or consolidant and then with different forms of dressing, but as yet there is little scientific work in the field. It is important before applying a leather dressing to remove the old dressing and clean the binding, using something like white spirit which is not going to harm any dye present. A hard consolidant will not work where flexibility must be preserved, but as yet, attempts to find a flexible polymer which will penetrate the leather without straining it too much and will form a film inside the rotted leather, encasing the fibres, have not proved successful.

(C. Clarkson, A. Cains and B. Haines)

Reduction of shrinkage temperature as a result of ageing

The shrinkage temperature of undamaged vegetable-tanned leathers will be 75-85°C, and vellum and parchment can be even lower, at about 60°C. If the leather is deteriorated in a gas chamber (this was the only experience Haines had of the problem) the shrinkage temperature of vegetable-tanned leathers can drop to around 65°C. This means that there is not much leeway if any form of heat treatment is proposed. Before a maximum temperature for any form of heat treatment could be decided on (Richard Smith suggested a figure of 50-55°C), the time of the treatment must be taken into consideration. Shrinkage temperatures, as given here, have been judged by placing a piece of leather in water and measuring it at a standard rate of raising the temperature. It may therefore be said that a level is safe for so many minutes at 60°C but that prolonged treatment at the same temperature could damage it.

(R. Smith and B. M. Haines.)

Alum-tawed skins

Attention was drawn by Roger Powell to so-called alum-tawed skins which, on examination, turned out to have very little alum in them and neither looked nor handled like traditional alum-tawed skins, and also contained synthetic tannages. This reinforced the need to know by what processes leather had been prepared, but whilst some tanners are reluctant to supply this information, many purchasers were completely ignorant of the qualities that they should be looking for. Although not a complete tannage, alum tawing has been

established both through experience and testing as a process by which extremely durable skins can be produced. It remains, however, vulnerable to deterioration through washing out the salts if it gets soaked in water. If this is carried out completely, the end product will be a raw skin. However, experience after the floods of Florence showed that not all the alum salts were removed by immersion in water and subsequent drying. The skins would go hard (the salts act as an interspacing between the fibres and give a certain amount of flexibility to the skin) but would remain quite durable. Experiments at the same time with rehydrating the water-damaged skins, dessicating in acetone and then staking indicated that it was possible to restore the texture and flexibility of hardened skin, and that oils could be worked into the skin to improve this. Above all, the skins remained extremely strong and able to withstand manipulation and working.
(B. Haines, C. Clarkson, R. Powell and A. Cains)

4.2.3 Minimizing deterioration of bookbinding leathers in polluted atmospheres

Betty M. Haines

The mechanism of deterioration of leather due to atmospheric pollutants is still not fully understood. The absorption of sulphur dioxide from the atmosphere and the increase in the acidity of the leather is a contributory factor but other pollutants such as oxides of nitrogen may well be involved.

The main mechanism of deterioration is likely to be an oxidative reaction. Bindings containing no tanning materials such as vellum, or leather prepared with mineral tans such as aluminium or chromium are resistant to deterioration. Vegetable tans appear to play a positive role in deterioration, but they produce a leather with properties required by the binder.

Vegetable tans of the hydrolysable type such as sumach produce a leather that is less readily deteriorated than leather tanned with vegetable tans of the condensed type, i.e. mimosa.

Today binding leathers are likely to be tanned first of all with a vegetable tan, and retanned with the aluminium or chromium salts. The former retannage produces the more durable leather.

At the present time there is no reliable guide for the purchaser requiring a durable leather. A gas-chamber test would appear to be the most appropriate accelerated laboratory test but conditions have not been standardized.

The most appropriate action would seem to be that binding leathers should carry information as to the tanning materials used.

The covering of books makes somewhat similar demands on leather as the covering of furniture in that the leather needs to mould well to the shape of the object being covered, and it is required to be durable in the face of atmospheric pollutants, but for a far longer period of time than leather in any other end use.

The mechanism of deterioration has proved a fascinating and challenging subject to the leather chemist, but those concerned with the conservation of bindings are faced with the dilemma of medieval bindings remaining in a good state of preservation alongside twentieth-century bindings in an advanced state of deterioration. This marked disparity between the performance of early and current bindings was causing concern as early as 1850, when the first investigation began and leather rot was associated with sulphur dioxide in the atmosphere.

In 1924 Faraday Innes, in collaboration with the then Library of the British Museum, began a series of investigations which extended over ten years. He confirmed that absorption of sulphur dioxide from the atmosphere accelerated decay, and found that rotted leathers contained as much as 5.0-8.0% sulphuric acid. [1]

He was able to show which tannages gave the most durable leathers and which should be avoided. Up to the last few years bookbinding leathers were either alum tawed or tanned with vegetable-tanning material. The latter are extracts from bark, pods, seeds and leaves. They differ in chemical type depending on their origin and impart different properties to the leather. Vegetable tans may be divided into two main types — hydrolysable tans and condensed tans. Hydrolysable tans were found to give a more durable leather, condensed tans a less

durable one, in the face of atmospheric pollutants. The natural salts present in vegetable-tanning materials were found to act as buffers. Surface dyeing of the leather that left natural salts in the leather gave a more durable leather than one that had been dyed by immersion in the dye bath, which removed the salts. This observation led Innes and others to advise the addition of buffer salts such as potassium lactate or potassium citrate to binding leathers to act as buffers against sulphur dioxide in the atmosphere.

Absorption of sulphur dioxide is retarded if the surface of the leather is coated with a relatively impervious finish. However, for good adhesion of the gold leaf, binding leathers should have either no surface coating or a thin coating consisting of casein. Bookbinding leathers are therefore particularly vulnerable to this source of damage.

By 1935[2] the evidence obtained from the examination of breakdown products extracted from rotted leathers indicated that the mechanism of leather rot was an oxidative process accelerated by acidity. Hence in the 1930s many laboratory tests were developed which were claimed to give a prediction of service life for bookbinding leathers in polluted atmosphere. One of these was the PIRA test,[3] which aimed at bringing about rapid oxidative degradation in the leather by applying sulphuric acid and then hydrogen peroxide to the leather. Because some tannages, which experience suggested were resistant to polluted atmosphere, behaved well in this test, leathers were sold bearing a stamp to indicate that the leather had passed the PIRA test.

A long-term storage trial was set up in 1931 to check on the validity of this test and the importance of the many factors that were considered at that time to have a bearing on leather decay. Leathers of various tannages were used to bind books which were held at the British Museum Library in the heavily polluted atmosphere of London and at the National Library for Wales at Aberystwyth, where atmospheric pollution was slight.

By 1970,[4] skins that contained no tanning material at all, such as vellum parchment or raw skin dehydrated with acetone, showed no sign of deterioration at the end of the trial, nor had they accumulated significant amounts of sulphuric acid. Mineral-tanned leathers, either chrome tanned or alum tawed, behaved in a similar way. Of the vegetable-tanned leathers those tanned with sumach showed little decay. Leathers tanned with other hydrolysable tans were more resistant than those tanned with condensed tannins: the latter had generally reached an advanced stage of deterioration after twenty years' storage.

Unfortunately, the trial also cast grave doubts on the validity of the PIRA test as a prediction of performance. It was, in any event, limited to the evaluation of pure vegetable-tanned leather.

Generally, the better performance of untanned or mineral tanned material indicates that some vegetable tans play a definite and positive role in the degradation process.

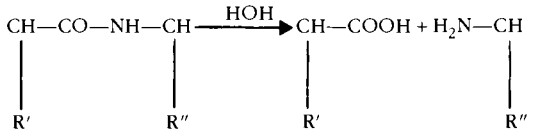
Mechanism of deterioration

The mechanism by which deterioration proceeds is not fully known although the influence of certain factors has been well established. For example, it is accepted that sulphur dioxide in the atmosphere contributes towards leather rot. Sulphur dioxide oxidizes to sulphur trioxide, providing a source of sulphuric acid. The catalytic role of metal contaminants of the leather in the oxidation of sulphur dioxide is open to question, since workers at Harwell have shown that sulphur dioxide, once it is absorbed on a surface, will be oxidized to trioxide within two weeks in the absence of metals. Consequently the beneficial effect of applying sodium pyrophosphate to the leather is also open to question. The benefit, originally demonstrated by the PIRA test, may well have been derived from the buffering action of the salt rather than its sequestering action on the metal contaminants.

Deterioration appears to depend on acid conditions within the leather. At the end of the long-term storage trial the sound leathers were at a pH greater than 2.8 and rotted leathers at a pH of 2.5 or below.

Consequently it is essential that a binding leather should at the outset have a pH above 3.5. The inclusion of buffer salts will serve to maintain this pH level. The long-term storage trial clearly demonstrated the protective action obtained by adding buffer salts such as potassium citrate or lactate to vegetable tanned leather.

Hydrolytic breakdown of the peptide linkage in the collagen molecule occurs in the following way:



The rate of hydrolytic degradation is highly dependent on pH, as shown by the graph in *Figure 4.27*. However, at the low relative humidity of 60% or less generally found in libraries, hydrolytic degradation is slow.

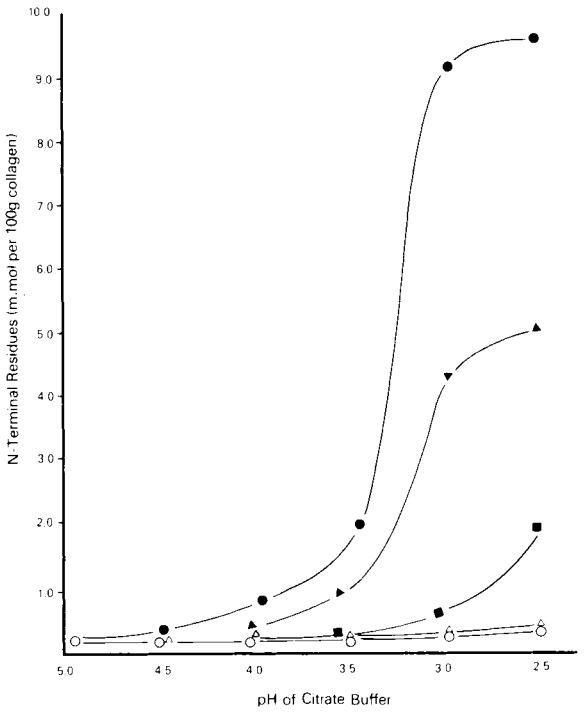


Figure 4.27. N-terminal residues (indicative of degree of hydrolytic degradation) released by storage at various relative humidities at 40°C for 8 weeks. O—O 100 per cent RH, Δ—Δ 40 per cent RH, ▲—▲ 85 per cent RH, ■ — ■ 75 per cent RH, ●—● dry.

There is another mechanism by which the peptide linkages in the collagen molecule can be attacked — this is by oxidation which occurs in the following manner:

$$\underset{\substack{|\\R'}}{CH}\!-\!CO\!-\!NH\!-\!\underset{\substack{|\\R''}}{CH}\!-\!CO \xrightarrow{O} \underset{\substack{|\\R'}}{CH}\!-\!CO\!-\!NH_2 + OC\!-\!\underset{\substack{|\\R''}}{CO}$$

The breakdown products extracted from the rotted leathers of the long-term storage trial point to this being the main mechanism of deterioration.

Although absorption of sulphur dioxide from the atmosphere and the acidity of the leather has been shown to be related to deterioration in binding leathers, other pollutants may well be essential to the mechanism of breakdown but they have never been studied in any depth.

Sulphur dioxide and oxides of nitrogen form the greatest proportion of atmospheric pollutants, but in the presence of sunlight, oxides of nitrogen and hydrocarbon react to form new products such as ozone, nitrogen dioxide and peroxyacetyl nitrate, all of which could be involved in the oxidative degradation of the protein.

At the present time the most reliable accelerated laboratory test by which durability can be evaluated appears to be a form of gas chamber incorporating a flame and a source of sulphur dioxide, but test conditions have not been standardized.

It used to be said that leather bought from Nigeria was going to be durable. At the present time there is no guarantee that a durable leather will be obtained by buying it from any particular part of the world. The traditional durability of Nigerian leathers derived from the fact that the type of vegetable tannin that was indigenous to the country was perhaps of the hydrolysable type. Now tanning materials are being extracted and sent all over the world, and the best guide for the purchasers of a binding leather where durability is important is knowledge of the tannage that has been used. There is no guarantee of durability in purchasing leathers from a particular region of the world which once held a reputation for durable leather, as tanning materials are now being used that are not indigenous to that country with the consequence that the performance of the leather may well change.

To obtain goat leather, it will have to be brought into the UK already tanned, as very few raw goatskins (broke skins) are imported. The native tannage which has been applied must therefore be accepted. Some manufacturers in the UK will extract all that vegetable tan and will then retan with a vegetable tan (sumach) which the long-term storage trials have indicated will give a durable leather. Alternatively, a vegetable-tanned leather may be retanned with mineral salts, and it is known from work done recently in the UK and in America in the 1930s that if it is retanned with aluminium salts. it is likely to be more durable than if it is retanned with chromium salts. It is therefore important to know what tannage has been applied to any particular leather. If, for example, a leather tanned with a mixture of vegetable and chromium tans is treated with potassium lactate, the chromium tans are likely to be stripped out.

It must be remembered that leather technology is constantly changing and new products can be used to obtain a certain desired character in the leather, but their influence as far as durability is concerned is not known. Selection of dyes is sometimes on the basis of initial colour, not permanence. Unfortunately there is little commercial interest in research for leather having extremely long periods of durability as the market is small.

It is this unsatisfactory state of affairs that has prompted current investigations into the deterioration of binding leathers and the preparation of durable leathers that have the properties required

by bookbinders. On the basis of the current knowledge, apart from genuine sumach tanned leathers, it would seem that binding leathers tanned first with hydrolysable vegetable tans and then retanned with aluminium salts have excellent resistance to deterioration (as shown by gas-chamber tests). In general, craft binders have found it difficult to work with the more inherently resistant mineral-tanned leather.

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5.1
Photographic

5.1.1 The role of micrographics in the treatment of modern records

S. John Teague

Various types of microform are described and their growing use by industry and local governments, which will soon make them the concern of the archivist, are discussed. The author also outlines the factors which must be taken into account by the archivist considering large-scale use of micro form, and indicates some of its advantages and drawbacks.

The problem of our lack of experience regarding the stability and longevity of various types of microform is discussed and desirable conditions of storage described; silver halide film is recommended as 'archivally permanent', and some (1980) prices given.'

Resistance to microform on the part of both archivist and user must be overcome so that full advantage may be taken of its numerous assets.

When one feels somewhat overwhelmed by the problems of conservation of library and archive material on paper, it is all too easy to convince oneself that a panacea is to hand and it seems that some conservators might too readily cast photography in that role. Therefore we shall try to outline factors upon which the stability of photographic records rest. Also, we are sure that the conservators should always be aware of the desirable longevity for the particular archive material being conserved. We must be realistic, all our work costs money and additionally there is the opportunity cost of the alternative archive work that might have been done instead. Therefore it is vital to seek that technique and material best suited to the particular task in hand. Thus we shall discuss medium and optimum life spans of photographic records, storage requirements, implications for reading and other consultation areas, costs and additional benefits accruing from the non-paper media. But in all this the author is speaking in a practical sense as a librarian, as a user of archive material, not as a technical expert in photochemical science.

Let no-one doubt the importance of photographic materials in preserving records of our heritage. Such materials will be a continually growing presence in our libraries and archives. Thus we are concerned with *processed* photographic film, plates and paper. We are not, of course, interested in the short term, for all the materials discussed, are, if properly processed and stored, safely in either the medium or the optimum range of probable longevity. By medium range let us assume ten to thirty years minimum useful life and optimum in excess of one hundred years. it is not wise to define things more closely, for even the British Standards Institution definition of *archival record film* merely requires 'a photographic film composed and treated so that under optimum storage conditions it is suitable for the preservation of records having permanent value'. All things have their season! Don M. Avedon of the National Microfilm Association of America wrote 'Archival permanence refers to the ability of the entire processed microfilm to retain its original characteristics and to resist deterioration over time'.[1] By *entire processed microfilm* he meant the base material, the emulsion and the processing used.

The types of processed photographic materials with which we are concerned can be very briefly

described as to sensitized material and format. The film base will be safety film manufactured either from one of the cellulose esters or from polyethylene terephthalate. Cellulose nitrate film base has not been used since 1951, but would, in any case, be unacceptable in an archive or library. The fire-safety indication covered by the term 'safety film' implies difficulty in ignition and slow burning when ignited, together with very limited emission of toxic oxides in burning.[2] Sensitized materials in current use are the silver halide, diazo and vesicular groups. We will refer to these again later, but the only archivally 'permanent' film is silver halide that has been properly processed.

Film formats that concern us are roll-film, microfiche, microfilm jackets and aperture cards. All the film formats can be either negative or positive and they are all *microfilms*. To get that term out of the way; all filming involves a photographic reduction, usually to the extent that the microfilmed text cannot be read with the naked eye. The term *microform* is commonly used to comprehend the whole range — for *microfilm* specifically conjures up the idea of a roll of film. Reading microforms involves the use of reading equipment that will display a legible image of the original at full size or larger than the original.

The most common microfilm is roll film. It comes in 30 m rolls and is normally either 34 mm or 16 mm wide. Usually on standard reels it can be on proprietory holders. (These holders, cassettes, cartridges or magazines are incompatible as between types and makers.) Microfiches are sheets of microfilm normally of international standard A6 size, 150 mm by 148 mm, and the images are in rows, fourteen rows horizontally and seven rows vertically, making 98 images. Microfilm jackets are film holders, basically of two transparent sheets sealed together to provide rows or solts in which to insert cut strips of roll film. Thus the channels can be either 16 mm or 35 mm wide or a combination of both. Aperture cards are 80-column punched data-processing cards in which a rectangular hole or holes are cut for either 16 mm or 35 mm film to be inserted. Thus these cards can be visually coded for hand or machine sorting and displayed on reading equipment for examining the content of the film insert.

The major part of the film presently in archive offices may well be positive 35 mm roll microfilm with some 16 mm. The size of the original is the major determining factor as to the film format chosen. 35 mm is ideal for large historical records, newspapers, maps and plans and 16 mm for office documents and publications. It follows that either of these film sizes is suitable for full systematic or selective rearrangement in any chosen order on aperture cards or microfilm jackets. Microfiche are suitable for all sorts of reports and publications, particularly those up to several hundred pages in length, for they are much easier to handle than roll film. We will not enlarge on this as there are several brief outlines available, such as the author's own *Microform Librarianship*.[3] Computer Output Microform is photographic output from the computer directly on to film (without ever having been set up and printed in the usual sense). COM fiche is the growth medium in commerce and it is 209-frame format, that is, 209 pages of text per fiche.

As to whether you have to bother with the modern media just because you are concerned with modern records, there can be no doubt. The Local Authorities Management Services and Computer Committee report on *Computer Output Microform in Local Government*[4] gives a very clear indication of a growing flood of microform material that will become the province of the archivist in due course. Of 74 authorities returning a questionnaire, 47 were using COM and ten were about to use it; and each COM-using installation had an average of five applications for which COM was used. Microfiche was the most popular type of microform, with 90% usage. The normal production arrangement was use of a bureau; that is, the employment of a specialist firm to carry out the filming and processing. The applications listed, ranging from financial records of all kinds, valuation rolls, ratepayers' name and address lists, bonds and mortgage listings to electoral rolls, land-use surveys, magistrates' court records and population censuses, all generate material for the archivist. The major reasons given for the use of COM were space economy, easier document handling and distribution, cost reduction and saving computer time as compared with use of line printers. Autorities actually found a benefit in practice that proved much more significant than they had considered at the outset; this was improved data retrieval. This affects archivists in that all sorts of additional outputs can be arranged provided they are allowed for during the systems analysis stage; so our records can be more useful. As an example a computerized census survey could be programmed to yield listings by occupation, sex, racial origin, size of family or whatever. Cheaply reproduced computer output microform copies can also make records available for distribution to libraries and other public service points, thus aiding conservation at major repositories.

There are other implications stemming from the fact that some modern records become, in due time, archives of permanent interest and the fact that

modern reprographic methods make replication much less of a problem and certainly less costly than before. It is now more important to distinguish between the permanent archival aspect (as to the material format of the archive, as to storage conditions and as to access), and the consultation/search room/research library aspect. There is the 'film it and throw it away' school of thought which must be taken seriously. Space is at a premium and, what is more, fully air-conditioned, fire-resistant, secure space is even more so. Therefore the bulk of material housed in such expensive space must be very carefully considered and controlled.

Do we then go for smaller storage areas? If one has a vault housing silver halide archival microform records, certainly one can have daily use copies on cheaper material of shorter life (such as vesicular and diazo) housed in reasonably controlled library or search room conditions, handled appropriately, and on need, in many cases after thirty years or more of use, a replacement copy can be made from the original. But, of course, we cannot have this 'film it and throw it away' concept foisted on us against our better judgement! The serendipity or browsing method of research will always be vital, and we defy anyone to browse successfully or happily through filmed records! We assert without fear of contradiction that no filmed copy can be better than the original and often will be very much worse.

This does not mean that microfilm should not normally be the medium one consults in the record office for all pre-1900 documents and for any others of great intrinsic, historical, artistic or other value. Certainly the originals in these cases must be retained out of general use in the best controlled storage we can get. We are concerned with conservation, not destruction. We can, however, film and throw away even some Victorian printed sources provided, that they are not the last extant copies.

Stress must be placed upon the continuing need for calendaring and indexing records, for making these indexes available in typed or printed paper format for wider distribution. The point is that the modern, even more than the traditional, media rely for their utility on one being able to discover in an acceptable way what is there.

There is a role for microphotography in conservation in perfecting imperfect volumes in that plates or maps, coloured, or black and white, can be photographed from a perfect copy and inserted in a pocket in microfiche format in the imperfect volume. Xerography is probably best and cheapest for most textual purposes, its permanence being dependent only on the paper used, provided that the xerox machine is properly warmed up before use.

To the known startling current rate of acceleration of decay of paper and binding in our libraries and archives has to be added the problem of lack of knowledge about the longevity of the newer media. This lack of knowledge stems from a variety of causes, such as, for example, the very newness of the medium in the case of the magnetic disc, or from the changing composition of the materials used in processes such as photography. Laboratory testing based on accelerated ageing is no certain guide to longevity of materials in real life, but without it we would be in an even worse position. The materials currently used in photography to which we referred go back, in the case of the film base, to 1908 for cellulose esters and 1956 for polyethylene terephthalate, so our practical experience is limited and we rely on standards derived from laboratory testing. There are, however, glass photographic plates in excess of one hundred years old in sound condition in archival storage.

National and international standards relating to archival photographic materials lay down minimum standards as to ignition time, burning rate, emission of harmful chemicals in burning, viscosity retention, nitrate nitrogen content and lack of free acidity, layer adhesion, tensile strength, image stability, lack of curling, and freedom from residual thiosulphate. The purpose of standards such as *B.S. 5699*, 1979 (ISO 4331/2) *Processed Photographic Film for Archival Purposes* is 'to eliminate possible hazards to permanence attributable to the chemical or physical characteristics of the processed film. Some of these characteristics are the responsibility of the film manufacturer, some of the film processor, some are influenced by both'.[5]

The remaining risks to longevity are those arising from conditions of storage and usage. There are optimum conditions as to temperature and humidity and there is the obvious need for protection against the hazards of fire, water, fungus and atmospheric pollutants such as oxides of nitrogen, sulphur dioxide, ozone and dust. These conditions do not differ markedly from those requisite for paper-based records. If one achieves a relative humidity in the range of 15-35% and a temperature between 15 and 22°C, one can safely store photographic plates and film-based material (silver gelatine, colour, diazo and vesicular) as well as copies on photographic paper. Having ensured that production and storage are both in accordance with the appropriate standards it is necessary to see that quality control extends to matters such as density, contrast, completeness of filmed material,

focus and reduction ratio, for it is little use having a permanent but illegible film! There are harmful storage and usage habits that you will know about that need to be avoided in the case of film just as much as paper. Much packaging has a very short life and can contaminate. Use of paper clips, rubber bands and lacquered boxes is to be avoided. Anodized aluminium or stainless steel cabinets with on-edge storage without pressure on photographic surfaces and individual paper packets made from high alpha cellulose, pH neutral, are requisite.

Film meeting the required standard in all the particulars we have noted should have a useful working life of at least as long as 100% rag-stock paper. 'Archivally permanent' is regarded in terms of hundreds of years, we hope. A representative of American National Archives is on record as saying 'essentially the term 'archival' is synonymous with 'permanent' and the two are frequently used interchangeably. To us they have the same meaning: that is, 'forever'.

Colour films are not approved for archival use since they are known to fade over a number of years (10 — 30). As silver halide microform is regarded as 'archivally permanent' we should specify it for all except expendable material. Diazo is a much cheaper film stock and is not proven archivally to the same extent as is silver halide. However, A. R. Materazzi of the United States Government Printing Office asserts that 'under archival conditions, as presently defined, diazo fiche may not have the same degree of permanence as silver halide; but they will be usable for at least a hundred years or more'. 'Under conditions which actually exist in research libraries,' he goes on, 'both diazo and vesicular films are superior in resistance to wear and to biological attack.'[6] Nevertheless we would be wise, for a while longer, to specify diazo only for expendable copies. We can, however, accept Public Record Office and US Government Printing Office output on diazo to gain the advantage of cheapness, knowing that these agencies will ensure that there is a master copy available from which replacements for faded copies can be made. We should not use vesicular film for archival work until further research has ensured that destructive gases are not emitted in storage, as was the case with some early vesicular film. It has, in any case, to be stored separately.

Reading equipment for each type of microform needs to be acquired as well as reader-printer facilities. In considering reading equipment we should check that focus is maintained when the film or fiche is moved (do not trust the manufacturer: check in use in a library). We must require rotating image facility for film readers, variable luminance intensity for all our equipment, together with no hot spots on the screen, no fade at the edges, minimal noise and heat in use. We must check that the film or fiche is not scratched in use, that lens changing is as simple as using a switch, and that we have full-page viewing with full magnification back to the original size. The environment we provide for microform reading must be such as to encourage research and the reader should be able to control his or her ambient lighting, screen angle and seat height.

In archival records there is a legacy of badly filmed materials, either badly filmed from good originals or less than expertly filmed from poor originals (that is, stained, torn, faded, incomplete or whatever). To compound the error, the reading equipment in archive offices is often even worse than that in libraries, being old, poorly designed, noisy, glaring or glimmering and inadequately maintained by staff who apologize for its necessity amongst other, more acceptable, provisions. This situation is no longer tolerable; we must refilm where necessary and re-equip.

Problems have been highlighted, but so too we hope, have possible solutions. Film can certainly be held to be more durable than magnetic tapes or discs which can be erased electromagnetically. Indeed, we understand that 'floppy discs' are at great risk from magnetic sources and even from the cigarette ash of a careless operator. The growing tide of word-processing systems in administration will certainly present the archivist with this sort of material that will either need vast arrays of differing electronic reading apparatus, systems and programming staff, or will need to be transferred into one standard medium before becoming the concern of the archivist. The simplicity of retrieving information from the microform, however, makes its continuing presence in archives likely.

As to costs, a microfiche silver halide archival master costs £7 and copies, if one is buying 50, cost 21p each. If one has non-archival diazo copies, these are 13p each. Microfilm costs £6 per 100 exposures per 35 mm reel, filming and processing. The prices of all these are subject to discounts for quantity or contract as are aperture cards or microfiche jackets. Xerographic copies, depending on size, cost between 3 and 5 pence per sheet.

Perhaps the 'received' view of archivists of the place of microfilm in archives has been the cautious approach displayed by Michael Cook in his book *Archives Administration*.[7] Briefly, this view is that space saving alone is unlikely to be a sufficient reason for adopting micrographic techniques in archives, although it may often be the necessary spur to thought in that direction. Space saving in a high-cost accommodation situation coupled with a

long retention requirement and the absence of cheaper outhousing facilities are rather grudgingly stated as prerequisites to taking the awful step of microfilming. To be fair, Cook goes on to appreciate the point that microreprography can facilitate additional service advantages such as to multiply access with minimal additional cost and early provision of a filmed archival copy of 'active' administrative documentation of a public body.

Reprography can help by providing the means of using expendable copies whilst safeguarding originals. Whilst xerography is useful here to a limited extent, microfilming is the better technique. The constant handling of the original involved in the provision of xerographic copies introduces a more damaging form of use than normal consultation. With film, once filmed, film copies can be used both for consultation and for providing either paper photocopies or diazo duplicates.

To sum up, the use of micrographics is growing whether we like it or not, but user resistance is still a reality. Microforms in archives and libraries can save 95 — 98% in storage space (but require some addition to reading space, as each microform reader takes up a full reading space and at least one third extra table space will be required for note-taking from the displayed source). They have relatively low reproduction costs and cheap and rapid distribution facility. They can, by having the data stored in the computer at the time of production, bypass printing altogether and be directly output onto film. Microforms have long life when used and stored correctly. Electronic systems of information storage and retrieval are now being cast by some people in the role of taking over both from the microform and the printed paper book and document. Electronic records are not, however, 'archival' and electric power may not always be readily available, and in any case a multi-media situation is much more likely.

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5.1.2. Problems in the conservation of silver gelatine prints

Alice Swan

Silver gelatine printing paper has been the predominant photographic printing material since the turn of the century, but very little is known about how ageing affects it, and what the most suitable conservation treatments are.

With some photographic material, reproduction is the answer for preservation purposes, but where the original print is an object of value the problem is far more difficult.

Damage is caused either by chemical instability in the print or by external factors such as bad mounting. Until now, restoration literature has concerned itself only with the first type of damage, and even so, the treatments suggested, while effective for more modern material, are chemically inappropriate when applied to older prints. Much more research is needed into the problem.

The conservation of photographs is an extremely new field. It is only in the last twenty or thirty years that photographs have been recognized as important objects of aesthetic and historical value and that their condition has become of concern to museums, archives and collectors. Very little research into the characteristic deterioration processes has yet been done — certainly not enough to generate sound conservation treatments; and those few treatments which have been published in the past were developed for use on new materials, and prove to be damaging when applied to irreplaceable and age-weakened prints.

Compared with the traditional artists' printmaking materials, photographic printing materials are complex and unstable, consisting of a reactive image of finely divided silver particles embedded in a fragile colloid layer, bonded to a paper support which frequently exhibits poor archival characteristics. While paper conservation provides a useful set of techniques and many restoration materials for working with photographs, the conservation problems of the paper constituent of photographs are frequently mild compared with the problems of the silver and colloid constituents. Each of the three constituents sets limits on the treatments that are possible for the other two. Thus, for example, bleaching, a common paper treatment, cannot be applied to photographs because the silver constituent is easily oxidized.

Introduced in the 1870s, silver gelatine printing paper has been the predominant photographic printing material since the turn of the century, and therefore the great majority of prints in many photographic collections are silver gelatine prints. In the paper which follows we will describe the structure and materials of silver gelatine papers, concentrating on the laminate structure of the paper and the microstructure of the silver image, and will relate these structures to characteristic deterioration processes and conservation problems. Finally, we will discuss the utility of one of the most common, current conservation treatments.

Identification

Of the many varieties of silver gelatine papers which have been manufactured, only the early papers present difficulties in identification. Such papers

frequently replicate the appearance of contemporary albumen and collodion papers. Gelatine emulsions, however, can be readily identified by placing a droplet of water on the print surface and observing the rate of absorption and the amount of swelling under the microscope. Collodion surfaces are impermeable to water (though water may be absorbed into the substrate through breaks in the surface), and albumen emulsions swell very little. Aged albumen coatings have a characteristic network of small fissures and cracks in the layer which provide straightforward visual identification under the microscope. Destructive but specific microchemical tests, such as the hydroxyproline test[1], can be used to supplement visual identification as a training device, but are seldom needed in practice.

Laminate structure of the papers

The structure and thickness of the layers composing a printing paper greatly influence its physical properties. Silver gelatine papers generally consist of a paper base, a gelatine-barium sulphate underlayer, the silver gelatine emulsion and a protective gelatine supercoat.

The paper base of earlier gelatine papers was composed of rag fibres, but present printing papers are generally made from wood pulps, sulphite pulps being the most frequently used. The α-cellulose content should be very high — Glafkides claims that less than 4% of the fibre content may be hemicelluloses[2]. The fibres are usually highly beaten and very short. The pulp must be very pure and free from metals, especially iron and copper, as well as from other photographically active materials, such as halides and reducible sulphur. Photographic papers must be able to withstand long wet-times and much handling while wet, as well as exposure to bases (the pH of developers is frequently 11 or 12) and acids (fixing solutions usually have a pH of about 4). To provide such chemical and water resistance, the paper is generally sized with starch or gelatine alum-rosin, and melamine-formaldehyde, which are added to the pulp as internal sizing. Dyes and kaolin are frequently present for colour and opacity.

The thickness of the paper bases varies widely according to the application, from the thin 'document' papers, measuring about 0.064 mm (2.5 mil), to 'double-weight' card papers, measuring about 0.38 mm (15 mil). Dimensional stability has been considered very important since the space distribution of the image frequently represents 'real' space, and should not change significantly as a result of processing or with humidity fluctuations. For most photographic papers expansibility is within 0.004% and 0.014% size change per percentage change in relative humidity. The papers are all machine made and have a prounounced grain[3].

The paper base is first coated with a layer of gelatine containing finely grained baryta (barium sulphate) to give an opaque, smooth, white surface upon which the emulsion can be evenly coated with good adhesion. Since the emulsion layer must be of a uniform thickness to record accurately the densities of the negative, surface modifications designed to produce a matt, glossy or embossed surface on the finished paper are made on the baryta layer. For glossy surfaces, very finely divided baryta pigment is used, several layers of the coating are applied to build up thickness and the coated sheet is calendered. For matt surfaces, the baryta pigment is coarser, the layer thinner and the sheet uncalendered. The baryta layer also contains gelatine hardeners, such as alum and formaldehyde, as well as dyes or optical brighteners. After coating, the paper is usually aged to allow complete hardening of the layer.

The light-sensitive layer of the laminate, incorrectly but immutably termed the 'emulsion' is coated next. In general, silver gelatine emulsions for printing papers contain less silver and are coated more thinly than film emulsions; since they will be viewed by reflected rather than transmitted light, only half the optical density will produce about the same absorbance. They are also much 'slower' emulsions, since a much longer light exposure is desirable for printing than for negative making. The lower speed allows them to be 'fine grain' emulsions; the size of the original silver halide crystals and the later, metallic silver particles is very much smaller than it is in films, which must have larger crystals to obtain increased light sensitivity. Paper emulsions utilize silver chloride and bromide, either singly or mixed, and, unlike film emulsions, generally do not contain silver iodine. Major criteria for the formulation of paper emulsions are image colour and contrast control, rather than speed and granularity, as is true of films. The range of colours producible in a silver image by controlling the size and structure of the silver particles is quite large, extending from warm red-browns through bluish-blacks. In addition to the silver halide crystals in the gelatine matrix, the emulsion contains gelatine hardeners and various additives to control its shelf life and developability.

When the emulsion has been coated and allowed to set but not to dry, a very thin final coat of gelatine with hardeners is applied to provide surface protection to the emulsion.

This is the most common structure of silver gelatine papers; however, in the century that these

papers have been manufactured there have been many variants. Many papers do not contain a baryta layer, the emulsion being coated directly over the paper base. Such papers, common at the turn of the century, usually have matt surfaces, and the pattern of the upper fibres of the paper can be seen in the surface of the emulsion. Abrasion of these papers frequently removes silver density in the pattern of the superficial fibres, and may even displace individual fibres if the emulsion is very thin. Supercoat layers have often been omitted, especially since their coating presented technical difficulties. Frequently a 'matting agent' consisting of starch grains or colloidal silica has been added either to the emulsion or to the supercoat. The common recent variant, resin-coated paper, includes a polyethylene coating over the back and front surfaces of the paper base, and the emulsion is coated directly on the polyethylene. It should be noted that these papers are not time-tested materials, and that some of the manufacturers have stated that resin-coated papers have not been recommended for archival applications.

Conservation problems related to the laminate structure

The expansion and contraction of the different layers with changing humidity is not identical: the gelatine emulsion expands much more than the paper base, and the baryta layer, with its large content of dimensionally stable mineral, probably lies between the two in expansibility. Even in prints where the drying process has been ideal, producing a flat print with minimal tensions, the sheet will curl with fluctuations in humidity, with the emulsion inside the curve at low humidities and outside the curve at high humidities. Since drying is seldom ideal, or humidity even, prints frequently curl non-uniformly, producing a variety of local deformations which are considered unacceptable in art collections, given the current aesthetic of photographic surfaces as 'clean', smooth, machine-made and flat. The amount of curl is controlled by the comparative thickness of the layers, the stiffness of the support, the method of paper making and drying of the coated sheet, the drying method after processing and the conditions of storage. Recent and minor local plane deformations can be flattened by humidifying the print and then pressing it between photographic-grade blotters under a glass sheet, but the print must afterwards be kept flat in an environment of even humidity or deformations will recur. Storage facilities for photographs clearly require humidity control, for the retention of flatness as well as for the stability of the silver image.

The problems of curling have been frequently dealt with by adhering a print to a more dimensionally stable, rigid, cardboard mount, usually by dry mounting — that is, adhering the print with a heat-set adhesive in a heated press. This mounting method has exhibited several problems including the great difficulty of later removing the print from the mount, the deleterious materials which have been favoured as mounts and the inherently damaging effects of the heat and pressure incurred in the mounting procedure. But beyond these well-known problems, dry mounting increases the differential of expansion and contraction between the front and back of the laminate, since it adds another, less reactive layer at the less reactive side. This causes greatly increased tensions in the emulsion with high or low humidity or with fluctuations. The author recently examined a silver gelatine print from the mid-1960s which had been mounted to a rigid board. The print had been stored at low humidity, seasonally cycled with more normal humidity, over a number of years, and the contractive forces on the emulsion had become so large that the emulsion had pulled up, taking with it the baryta layer and the top half of the paper base which it had split into two layers, leaving the lower half of the paper adhered to the mount; the separation had occurred along one whole end of the mounted print.

The opposite situation is commonly seen in dry-mounted prints which have been stored at high humidity. Dry mounting usually attaches a print and mount while both are at minimum expansion, especially if the mounter has 'pre-heated' the print and mount before attachment 'to prevent curling'. When such a laminate is exposed to high humidity, the much greater expansion of the print frequently separates the photograph from the mount in uneven waves and bubbles. The gelatine layers must expand or contract in response to humidity change, and the weakest bond between expanding and non-expanding layers will fail — usually at the dry mount tissue/mount interface.

Because of its layered structure, any bending or flexing of gelatine prints puts great tensile and compressive stress on the exterior layers, cracking emulsions and creasing and breaking paper layers. This structural lack of flexibility leads to much damage in handling. It seems necessary that the housings and mats devised for gelatine prints always provide rigid support.

The emulsion is frequently the most brittle layer of gelatine prints. The group of photographs in which this author has seen the most embrittlement and cracking is that of 'ferreotyped' glossy prints

from the 1930s and 1940s. Such photographs require special protection against flexing or bending in handling. It is unlikely that ferreotyping (drying the wet print with its emulsion moulded against a smooth and usually heated surface) itself contributes to the brittleness of an emulsion since it dries the emulsion in a highly stretched state, setting in much tension. Additionally, since adequate hardening of the emulsion is critical to prevent the print from sticking to the ferreotype plate, overuse of hardeners may be involved.

The larger expansive and contractive forces of the emulsion increase the difficulty of mending a break in an emulsion at a tear, crack or loss. Such a break tends to pull itself further apart, even under conditions of small humidity change. The emulsion sometimes separates from the baryta underlayer in areas of damage as well, again due to the uneven contractive stresses between the layers acting on an initially inadequate bond.

One frequently sees evidence of poor bonding between the emulsion and the baryta layer in older gelatine prints. Whenever edge damage to a print has caused chips of emulsion to separate from the baryta layer, or when there are signs of 'frilling' (separation of the emulsion from the baryta layer around the edges of a print during the original processing), we would particularly hesitate to dampen or wet such a print, since the increased tensions on the bond, caused by swelling differences among the wetted layers, will encourage further separation. Such separations are extremely difficult to reattach, even when very small. Among other difficulties is that of finding an appropriate adhesive: water-based adhesives swell the loose emulsion out of position, but one can hardly use a solvent-based adhesive since, either in use or in removal, it is likely to penetrate the surrounding area, preventing it from accepting water uniformly and causing further local differences in expansibility. Needless to say, the adhesive must also be chemically unreactive with silver and gelatine.

Very little is known about the optimal hardening of prints for maximum useful life; the long-term effects of the various hardeners have not been investigated. Hardening has been dealt with on immediate, practical grounds, as a necessary step to prevent emulsions from dissolving when processed at high temperatures or in chemical solutions which attack gelatine and has been measured by such gross physical tests as the melting-point temperature of the emulsion, and the weight with which a stylus can be loaded before it punctures a wet or dry emulsion. This author knows of no experimental work on the relation of hardening to emulsion brittleness, though commonsense would suggest that such a relation exists; and of no experimental work disproving the existence of a syndrome that might be thought of as 'overhardening'. It is known that formaldehyde, the hardener most frequently recommended for use in restoration treatments of gelatine prints, shows a marked tendency towards 'afterhardening' — that is, the degree of hardness in the treated emulsion continues to increase long after the treatment. Until more is known about the long-term effects of hardening, the use of hardeners (particularly the irreversible aldehyde hardeners) on irreplaceable prints seems unwise.

Nevertheless, when an older gelatine print is wetted one faces a possible swelling problem, caused by the frequently thicker emulsions and the unpredictability of hardening in older prints. Newer prints do not present the same difficulty since their generally thinner emulsions are more likely to have been hardened in manufacture (the major hardening for older prints was introduced by photographers in processing) and since they have been less affected by unpredictable ageing changes. Some indication of an emulsion's swelling tendency is given by its response to a droplet of water observed by raking light. Prints should be wetted slowly and treatments limited to cold or room-temperature solutions to control swelling. Conservators must also be aware of the complex effects of various chemical treatments on an emulsion's swelling behaviour, both in the solution itself and afterwards in wash baths: solution pH, concentration and temperature, as well as specific chemicals, have strong effects on swelling.

Drying gelatine prints is also a sensitive job since, when wet, the emulsions are swollen, soft and tend to stick and mould to other surfaces. In this state, extraneous materials are easily embedded in the emulsions (embedded fibres often provide an easily used clue in the identification of gelatine prints which are likely to swell excessively in wet treatment). Gelatine emulsions must be dried nearly to completion before any system of flattening involving contact or weight can be used. The frequently recommended method of drying prints face down on fibreglass drying screens causes surface damage: prints should be dried face up after water droplets have been carefully wiped from their surfaces. It is frequently impossible to utilize a photographer's original drying or flattening method because of the inherent damage or risk involved in the method; ferreotyping is a good example of such an unusable method, as are those of heated 'drum' dryers and dry-mount presses.

For some smooth-surfaced, unferreotyped gelatine prints, surface dirt can be removed by light, gentle cleaning with soft, non-abrasive erasers. This

should be done under a microscope with adequate magnification and raking light, since there are great differences in the ease with which gelatine surfaces can be scratched and abraded, depending on surface smoothness, emulsion hardening, the possible presence of surface 'matting' agents and many other conditions. Any eraser residue left on the surface should be removed by gently wiping the surface with dry, clean cotton wool. This cleaning step is only suggested because of the prevalence of extraordinary dirt layers on photographic prints caused by their typically poor storage conditions. It can abrade and wear the surface and should be avoided for less dirty prints.

Pads of cotton wool just slightly dampened with alcohol and other organic solvents are very helpful in cleaning print surfaces, though one must be careful not to use enough solvent to penetrate the emulsion, thereby spreading dissolved material which had been previously confined to the surface. This author avoids using water in surface cleaning because of its swelling effect, the certain penetration of the dirty water into the absorbant emulsion and the increased physical fragility of wet emulsions. Use of the frequently suggested ammonia solutions for surface cleaning seems particularly disadvantageous: not only is the swell of the emulsion and the penetration of the dirty solution maximized by the high pH, but ammonia forms a strong complex with silver, and if any oxidized silver is present in the emulsion (which is quite likely — as silver 'gelatine', for instance) it will be moved about locally, producing silver distribution patterns unrelated to the image, and causing non-image densities upon reduction by light or other reducing conditions. It would seem only reasonable that any use of ammonia should take into account its solvent action on silver salts, should take place uniformly (i.e. by immersion, not local application) and should be followed by a thorough washing.

The microstructure of the silver image

Silver gelatine papers can be divided into two classes based on the printing method used: 'printing-out paper' (frequently termed 'P.O.P.' in the manual literature) forms images solely by the action of light; whereas 'developing-out paper' ('D.O.P.') requires a much shorter light exposure which forms only very small metallic silver specks on the silver halide crystals, and these specks then behave as catalysts in the reduction of the crystal in development. All modern papers (with the exception of the 'studioproof' types) are developing papers, with the consequence that only developing papers have been investigated by modern techniques.

Gelatine printing-out papers, common from the 1880s to the early 1920s, have silver chloride emulsions prepared so as to give crystals of very small particle size. The emulsion contains a halogen acceptor — usually sodium citrate — to prevent the recombination of chlorine, produced in the light exposure, with the newly formed silver image. The silver particles so formed would be quite small and rounded. Printing-out papers were always toned — usually with gold, which modified the image colour from red-browns towards deeper, purple-brown tones; though formulas for sulphur and platinum toning are common in the mauals of the time, and even uranium toning is suggested. Gold toning had been standard processing procedure for albumen prints since the early 1860's and was known to provide greatly improved image stability. (Gold toning is still the treatment of choice for producing stable silver images — it is the recommended treatment for microfilms, for instance, wherever economically feasible). Since they required massive light exposures, these papers were always printed in direct contact with the negative. It is frequently possible to identify photographs printed by contact because of the small size of the reproduced negative grain.

Developing-out papers, introduced in the 1870s but not widely used until the 1890s, were designed for both contact printing and enlarging. They have most commonly been left untoned, though toning produces a wide range of colour variations and some types of toning convey added image stability. The most frequently used toning materials are sulphur, selenium and gold. Sulphur toning produces colours from warm brown to sepia to warm black and has been commonly and consistently used. Selenium toning produces warm black to red-purple-black tones and has been used in very minimal amounts by fine art photographers concerned about the subtle tonal gradation and permanence. Gold toning has been so expensive and closely associated with printing-out rather developing-out papers that its use for developed emulsions has been largely confined to archival applications since the mid-1960s.

Developed prints can be divided into two types, depending on the structure of the developed silver. Images produced by 'direct development' are formed by reduction of the silver of the silver halide crystals at the small, light-produced, catalytic silver specks, such that a fine filament or thread of silver is extruded at each catalytic site by the developer. Depending on the size of the silver halide crystal and

the amount of light exposure, there are frequently several catalytic sites on the same crystal. The result is a tangled mass of filaments, retained by the gelatine matrix in approximately the space originally occupied by the silver halide crystal. This type of structure is produced by active developer solutions with little ability to dissolve silver halide crystals. Such a structure has a large 'covering power', that is, a relatively small mass of silver gives a large optical density; and it exhibits uniform light absorption of all colours of visible light. Consequently the image appears neutral black and grey in colour. Print developers are usually of the direct development type.

The second type of image structure is produced by 'indirect' or 'solution physical development'. In this type of development the silver halide crystals are dissolved and metallic silver is deposited out of solution onto the catalytic silver specks. Consequently the developed silver particles are approximately spherical. This structure is produced by less active developing solutions with high solvent ability. This structure has relatively low covering power — a large mass of silver gives relatively low optical density — and the covering power decreases as the diameter of the particles increases past a certain threshold value. This structure shows a maximum light absorption at the blue end of the visible region of the spectrum, which produces a yellow or warm-toned image by reflected light.[4] Solution physical development has generally been avoided in the design of paper developers because the image colours it produces have been thought unpleasant. It is described here because it forms an important second silver particle structure.

Characteristic types of deterioration of the silver constituent

Of the two silver particle structures, the rounded particles are the more stable and their stability depends on particle size. The filamentary structure, which has a greatly increased ratio of surface area to mass, tends to recrystallize to the rounded, solid form unless the surface is stabilized by the presence of a strongly absorbed material such as sulphide, iodide or one of the numerous organic compounds termed 'blue-black agents' or 'anti-plumming agents' precisely because they promote the cold-toned filamentary structure and prevent recrystallization to the warm-toned, rounded structure under adverse conditions such as elevated temperatures in processing or drying. Among the rounded particles, smaller particles tend generally to recrystallize onto larger particles, though this process is dependent on many factors.

In a study of the stability of silver filaments, T. H. James[5] treated emulsions of filamentary silver by incubation at high humidity and by immersion in various salt solutions. He found that unstabilized filaments became shorter and thicker after a few days of incubation at 20°C and 100% RH, and recrystallized into rounded forms within a few minutes when immersed in solutions of salts forming silver complexes such as thiocyanate or chloride; whereas filaments stabilized with sulphide through normal thiosulfate fixing, or with iodide, changed much more slowly. Recrystallization was accompanied by reduced reflection density and by changes in image colour by reflected light. This author also notes that exposure to hydrogen peroxide causes recrystallization of filamentary silver. The structural change from filamentary to rounded form and from generally smaller to larger rounded particles is one very likely source of the density loss and colour shift towards yellow which are characteristically seen in older photographs.

Oxidation of the silver image is another major cause of density loss and colour change, which may occur evenly, locally (along edges for instance) or in spots. Reviewing the oxidants which had reproduced naturally occurring microfilm spots under laboratory conditions, Henn and Wiest[6] list atmospheric oxygen at raised humidities, the effect of which is accelerated by the presence of hydrogen sulphide, ammonia and sulphur dioxide; ozone and its derivatives, including the nitric oxides it generates in smog; and peroxides, which are commonly evolved from fresh paint, plastics, bleached wood (as in frames or cabinets), oxidizing metals and oxidizing organic materials, including paper. Indeed, the microfilm spots which had occasioned the research were eventually attributed to peroxides formed by the cardboard containers in which the films were stored.[7] McCamy and Pope[8] reproduced microfilm spots by exposing films to fumes from various oils, turpentine and powdered resin. Elevated humidity was found to be an important factor in spot formation: peroxide formation by paper, for instance, varies directly with humidity. Gelatine emulsions easily absorb water-dissolved gases due to their hygroscopic nature, and under conditions of humidity cycling might be expected to concentrate such substances. Weyde points also to the influence of the paper base, 'which has an astonishing storing effect by absorption of oxidizing gases'.[9]

In the microfilm spots, peroxides, active as oxidizing and as reducing agents, were thought responsible for both the oxidation and reduction of

silver in the spots.[10] The structure of the spots showed clearly that image silver had migrated through the gelatine matrix; it was thought to have migrated in an oxidized state and then to have been reduced at preferred nucleation sites, or to have been incorporated in a stable compound such as silver sulphide. Image silver was found to have formed a new structure of colloidal silver particles, appearing yellow and red because of the particle size, and often positioned in annular rings, sometimes around a centre; to have redeposited on the original filamentary silver particles, rounding and fragmenting their structure by recrystallization; to have formed highly reflective silver deposits on the surface of the emulsion (surface mirrors); and to have formed compounds such as silver sulphide, silver gelatinate and silver chloride.[11] Though the base materials, processing conditions and storage modes are different, the microfilm spot research offers an extremely helpful consideration of the mechanisms of the fading, yellowing and mirror formation that so frequently occur on photographic prints.

Both recrystallization and oxidation of silver images can be minimized by atmospheric control — especially the maintenance of low, even humidities. The current American National Standard for microfilm storage (ANSI PH5.4-1970) specifies that material for 'permanent' storage be kept at a relative humidity not exceeding 40%. Exposure to oxidizing materials such as peroxides and sources of peroxides must also be avoided.

The transformation of the silver image to silver sulphide is another major source of density loss and tonal change in silver gelatine prints. Silver sulphide, one of the most stable of the silver salts, is formed by any source of sulphide or reducible sulphur in the presence of ionic silver. It is formed as a monomolecular layer on the surface of image silver during fixation (or very shortly after), even with ideal processing, so reliably that the quantity present can be used to estimate the surface area of filamentary silver.[12] When a source of sulphur is available (such as residual thiosulphate left in an incompletely washed print, or the insoluble silver-thiosulphate complex left in a print by an exhausted fixing bath or one of the common sulphur gases in polluted air) oxidized silver will combine with it to form silver sulphide. A silver image which has undergone significant transformation to silver sulphide by these naturally occurring reactions has a 'faded' range of gradations of light yellow-brown, which are most obvious in highlight and midtone areas. Recrystallization of the image particles and optical effects caused by changes in the surface of the suphided particles are also important factors in the typically much-reduced optical density of the image. Increased sulphiding is frequently seen around the edges of prints if greater exposure of the print to sulphur sources has occurred at the edges, as happens, for instance, in the exposure of stacked prints or prints in albums to polluted air.

To minimize the sulphiding of silver images, oxidation of the image must be avoided, and the availability of sulphur from both intrinsic (residual chemistry) and extrinsic (air and storage materials) sources must be minimized. The problem of sulphur from intrinsic sources will be considered in a later section. As for extrinsic sources, sulphur gases are commonly present in polluted city air; air-conditioning systems for photographic archives need a filtering step to remove them. Unfortunately, some storage and restoration materials contain active sources of sulphur. This author has found acid-free interleaving papers, art papers, Japanese papers and polyvinyl acetate emulsion adhesives which contain active sulphur and cause silver sulphide formation in silver images. The use of such materials in repairing and matting photographs causes drastic local fading: Two unconnected cases have been recently seen — one where the active material was a sulphur-containing Japanese hinging paper, the other a sulphur-containing starch adhesive — where the image of the hinged print had faded from deep purple brown to pale yellow tones wherever the damaging hinging material had contacted the back of the print. In each case the hinges had been in place about two years when the fading was discovered, and the photograph had been stored under humid conditions, allowing migration of the sulphur source through the paper support to the emulsion layer. All materials to be used in the repair and storage of silver photographs must be tested, using a silver-tarnishing test.[13] Because trace quantities of active sulphur have a large effect, and because such quantities of sulphur are possibly present as a contaminant rather than as a constituent of materials, it is wise to test each separate batch or lot of materials.

Another very characteristic visual appearance of silver-image deterioration is the formation of reflective metallic surface deposits in areas of maximum silver content. This effect occurs more strongly in gelatine prints than in other types of silver prints, and so frequently as almost to typify older silver gelatine materials. Such deposits, present in the microfilm spots, are caused by oxidation of image silver, followed by its migration through the gelatine and reduction at the surface. When a sulphur source is available, the deposited silver is found in combination with silver sulphide. Such

deposits are commonly referred to as 'silvering' and are sometimes also called 'dichroic fog' in negative materials.

Problems with restoration treatments of the silver constituent

As noted previously, the restoration procedures for photographs that have been proposed in the past were not developed for, and have not been modified for application to irreplaceable and age-weakened prints; the great majority of formulas long antedate the present increased monetary values now assigned to photographs, belonging to an era which perceived photographic prints as replaceable and their collection as somewhat eccentric.[14] Utilizing powerful oxidizing agents, extremes of pH, irreversible and inadequately controlled deposition of image metals or the reintroduction of significantly unremovable contaminants, these restoration procedures need careful examination, evaluation, reformulation and testing for long-term effects before being applied to valuable prints. The restoration literature appears to be caught in a basic confusion between replaceable and irreplaceable prints; there are obvious major differences between appropriate treatment of one's own new prints and of valuable older prints on the basis of replaceability as well as the differences in materials and condition.

Indeed, the most commonly practised and least controversial of silver treatments, 'reprocessing', provides a clear example of the difficulties encountered in applying excellent routine procedures for one's own modern prints to irreplaceable older prints. 'Reprocessing' refers to treatment in a new fixing solution, followed by 'hypo-clearing' and 'hypo-eliminating' baths, both thiosulphate-removal treatments, followed by extended washing in water. The procedure is identical to that routinely followed for the archival processing of new prints, and is recommended throughout the restoration literature for all silver prints which have been tested with two 'easily used' test solutions and found to contain residual chemicals, i.e. the silver-thiosulphate complex and thiosulphate. It is this author's impression that reprocessing is currently practised frequently and routinely.

Residual silver-thiosulphate complex and thiosulphate, left in a print by an exhausted or poorly designed thiosulphate bath and by inadequate washing, are known to produce severe image fading and staining. The presence of these residual chemicals has long been identified as a particular problem for gelatine prints, promoted by the design of gelatine printing materials. The much greater mass of absorbent, retentive material per unit of image area allows much larger amounts of residual chemicals to be stored than is the case with the older printing materials. Comparing just the typical paper bases of salt, albumen and gelatine prints, it is clear that the thicker, highly compressed gelatine paper stock, with its heavy, synthetic, water-resistant sizing, allows less water movement through it and is therefore much more difficult to wash effectively. While extended vigorous washing is required for all silver printing materials which have been fixed in thiosulphate, and all of them fade and stain if washing is inadequate, gelatine paper prints have a much larger capacity to store residual chemistry, which under humid conditions slowly diffuses through the material, causing fading and staining capable of continuing over many years as it gradually reaches the silver image.

The restoration literature directs one to test for the presence of these residual with two tests, one for residual silver (Kodak Silver Test ST-1) and one for residual thiosulphate (Kodak Hypo Test HT-2), formulas for which are found throughout the restoration literature as well as in Kodak guides to black and white processing. However, there are several major practical problems in the use of these tests, which are entirely unaddressed in the restoration literature. First the tests cannot be applied to prints of value since both tests form unremovable silver sulphide stains (and formation of the stain constitutes the test), in the case of the thiosulphate test, by supplying free silver, and in the case of the silver test, by supplying free sulphide. A margin or other white highlight area must be used for the test so that the resulting stain can be seen and estimated adequately — but most older prints have no remaining margins, and some do not even have clear highlights in their pictorial spaces. Moreover, both test solutions are severe contaminants of silver images, such that even if the test results are negative the print must still be extensively treated to remove the test solution.

Further, the results of the tests may be misleading. Margins, for instance, are more likely to have been adequately fixed and washed than the centres of prints, since most processing and washing systems pass considerably more solution over edges than centres of prints, and solution flow is typically a limiting factor in these diffusion-controlled processes. Moreover, thiosulphate is retained more strongly in the emulsion in areas of increased silver content (the shadows of prints) than in highlights or margins. In a study of thiosulphate retention in microfilms, C. I. Pope found a nearly linear relation between thiosulphate retention and silver concen-

tration.[15] Additionally, uneven distribution of residual silver and thiosulphate is characteristic of extremely inadequate processing, such that a test result in one area of such a print will not necessarily match the test result from another area. Anyone who has worked with historical photographic collections has seen prints where yellowing and density loss were extremely uneven, with 'air-bell' shapes or corners or ends with greatly increased or reduced fading. Finally, the tests do not indicate the presence of the residuals in the baryta and paper layers of the print, though their absorption and retention in these layers is known to be a major part of the problem.

Even if the tests could be applied without incurring major damage to prints, and even if the test results were uniform and reliable, there would still be significant problems with the evaluation of results since there has yet been no attempt to establish acceptable stain levels for older prints or to correlate stain levels with eventual fading and staining. For example, the residual silver test always leaves some amount of yellow stain; a positive test result is described with unhelpful vagueness as more than 'a barely visible cream tint.'[16] Since a positive results directs one to a non-reversible treatment in an imperfectly removed, contaminating material (refixing), it would seem important to be able to differentiate more precisely between positive and negative results. Appropriate evaluation of the residual hypo test is equally uncertain. While varying levels of stain from the test (established by visual comparison with four yellow-brown patches of varying density provided in the Kodak 'Hypo Estimator') are listed as acceptable for various photographic materials in current commercial use, the Hypo Estimator instructions imply that materials for archival use must show zero stain. While this seems reasonable for new, physically strong and replaceable prints, it seems unnecessarily severe for older, already stained, irreplaceable prints — especially since these prints cannot usually withstand the long, vigorous, effective washes routinely used for new materials, and are also damaged by the commonly recommended alkaline peroxide hypo-eliminator baths; these are the two methods by which zero hypo test stains are achieved. Additionally, it is unclear in general terms how significant the achievement of zero hypo content will actually prove to be over long periods of time for prints where significant amounts of the silver image have already been transformed to silver sulphide. It is important that one be able to weigh the actual benefits of reprocessing an aged, somewhat faded print with a relatively small amount of unreacted residual chemistry, against the physical damages risked in the treatment.

In sum, a positive result from either test has meaning but disfigures a print and does not necessarily indicate treatment, while a negative result may not be believable but still requires treatment sufficient to remove the test solution (which, in the case at least of the hypo test, means reprocessing).

We should emphasize that both tests are very useful for evaluating the adequacy of one's own processing of new materials. Further, the residual silver test has an extremely important use in archives to identify prints which have been processed by 'stabilization', a fast-access processing method which chemically stabilizes non-image silver salts against light reduction, instead of removing them.[17] A stabilized print will give a dark stain with even a very small drop of the sodium sulphide silver test reagent. Such a print should be re-fixed and thoroughly washed before being added to a print collection, and any materials it was packaged in should be discarded. Both test solutions are unstable and must be mixed fresh periodically; a deteriorated sodium sulphide solution will give a false negative test result — a solution more than a week or so old should be tested against a print known to have been processed by stabilization.

With or without the inadequate tests, if one decides to reprocess an older print, what results might be expected? To examine the possibilities, the process of fixing must be reviewed. Silver gelatine prints are fixed in a thiosulphate solution (either sodium or ammonium thiosulphate) to dissolve and remove the unexposed and undeveloped silver halide crystals. This is accomplished by the formation of a series of silver-thiosulphate complexes. If silver bromide were the silver halide initially present, for instance, the reaction could be written:

$$AgBr + (S_2O_3)^{2-} \rightarrow Ag(S_2O_3)^- + Br^-$$
$$Ag(S_2O_3)^- + (S_2O_3)^{2-} \rightarrow Ag(S_2O_3)_2^{3-}$$
$$Ag(S_2O_3)_2^{3-} + (S_2O_3)^{2-} \rightarrow Ag(S_2O_3)_3^{5-}$$

The first silver-thiosulphate complex $[Ag(S_2O_3)^-]$ is readily formed, but remains absorbed to the silver halide grain. It is only slightly soluble in water and not very stable, breaking down in the presence of silver to form silver sulphide. If enough thiosulphate ions are available for equilibrium conditions to allow it, a second complex $[Ag(S_2O_3)_2^{3-}]$ forms which is soluble in water and more stable, and goes into solution, diffusing away from the silver halide crystal through the gelatine matrix. If enough thiosulphate ions are still available to satisfy equilibrium conditions, the third complex forms, also soluble and of increased stability.[18]

If a print is fixed in a bath with insufficient thiosulphate available, the second and third complexes will fail to form in significant quantity and the insoluble initial complex will remain in the emulsion. Because the relative amounts of the complexes are governed by equilibrium conditions, the first complex is always present in a used fixing solution and diffuses into the baryta layer and paper base, where it is strongly absorbed. This complex cannot be adequately removed by water washing and it breaks down to form silver sulphide, with the effect of discolouring the image. Images so affected show uniform yellowing which is most visible in the highlights. Recognition of this problem has led to the routine use of two successive fixing baths for the processing of new materials, and has been common practice among photographers concerned with the pemanence since the 1950s.[19] The residual silver test is intended to indicate the presence of this fixing problem, which is remedied by re-fixing in a fresh thiosulphate solution; though, of course, this must be done before a significant portion of the complex has decomposed.

If the print is properly fixed in a fresh thiosulphate solution such that all the silver halide is complexed and removed, the thiosulphate itself must still be completely washed out, since it is unstable in the presence of silver, eventually combining with image silver to form silver sulphide. Unfortunately, thiosulphate is strongly retained by the emulsion, baryta layer and paper base of prints, and it is not possible to remove all of it by washing, especially when it has been introduced in the standard acid-hardening fixing baths, since the acid condition of the solution, required by the alum hardener, causes ionic retention of thiosulphate in the gelatine. Treatment in an alkaline solution will help to remove thiosulphate, but also reduces emulsion hardening just when it is most needed — it is generally during washing steps that gelatine emulsions reach maximum swell and are most vulnerable to physical damage and frilling. The commonly used 'washing aids' (Kodak Hypo Clearing Agent is the best known) are salt solutions — usually buffered sulphite solutions — and displace thiosulphate in the emulsion, baryta layer and paper base by ion exchange. They require long wash times, considerably longer than manufactures' recommendations, and are not completely effective in removing thiosulphate, but they are much less damaging to gelatine silver prints than the commonly recommended 'hypo-eliminators', which are hydrogen peroxide-ammonia solutions. The hypo-eliminators function by oxidizing thiosulphate to sulphate; unfortunately they oxidize image silver as well, frequently causing perceptible bleaching of highlight areas. Their elevated pH causes excessive swelling of the gelatine, encouraging frilling of emulsion edges. Additionally, they have been found not completely successful in destroying all thiosulphate, and the short wash times recommended after their use may be inadequate.[20] Their use on valuable older prints should be avoided.

The rate of the breakdown of residual thiosulphate increases with increased humidity and the reaction continues until either the thiosulphate or the silver is exhausted. A print which has been completely fixed but insufficiently washed typically shows clean white highlights, but develops faded and yellowed image tones. The residual thiosulphate spot test is intended to indicate this difficulty, and it gives a positive reaction for all sources of active sulphur — the polythionate breakdown products of thiosulphate as well as thiosulphate itself. For new prints, this processing failure is remedied by additional washing, though for older prints the restoration literature seems to recommend a complete reprocessing treatment. Any treatment, of course, must be done before a significant amount of the thiosulphate has broken down to silver sulphide, since silver sulphide is not affected by washing or reprocessing.

While some reprocessing treatment is undoubtedly essential to the long-term preservation of recent prints filled with residual chemistry, reprocessing as outlined in the restoration literature (treatment in an unspecified fixer — presumably the standard, pre-mixed, acid-hardening fixer — followed by treatment in a washing acid, washing, treatment in a peroxide-ammonia hypo-eliminator, followed by a final wash) may be unnecessarily damaging to all prints and of no benefit to many. Re-fixing and the subsequent treatments required to remove thiosulphate might be expected to further erode the fragile silver image already partially transformed to silver sulphide, oxidizing, complexing and removing image silver in the acid-fixing bath, and oxidizing silver significantly in the hypo-eliminator bath.[21] Further, since re-fixing removes oxidized image silver, it will obstruct the future use of any silver reduction treatment which might be developed. Therefore it is of real importance to be able to identify prints which will actually benefit from re-fixing.

There are thus two sets of questions needing answers before the appropriateness of reprocessing any specific print can be known: the first would examine the levels of residual silver-thiosulphate complex and thiosulphate present after its original processing, while the second would examine the levels of unreacted residuals currently present

which will in the future break down, fading and staining the image, if left untreated. The rates of the breakdown reactions are very dependent on humidity and temperature and cannot be predicted as one might hope. Further, the mobility of residuals through the layers of prints is undoubtedly affected by the composition of the specific paper bases and baryta layers, making prediction less possible. The residual silver and hypo tests, which would supply some of the needed information, are too damaging to use. While close visual examination will establish that residual chemistry, initially present, has broken down, staining highlights or causing highlight and midtone fading, it gives no indication that a process has gone to completion, and it cannot predict a process which has not yet begun.

This author's own experience has been largely with 'fine arts' photographs, which were generally processed to the highest archival standards of their day, and where the large artistic, historic and monetary value of an individual print precludes the possibility of testing the adequacy of its processing with visually and chemically damaging solutions. Here, one can only address the problem with improved storage conditions, and fevently hope that better methods for determining residual chemistry will soon be developed. The situation may be considerably different in other sorts of collections, however. In collections, for instance, where the bulk of photographic prints are relatively recent, of low individual value as original objects, and have come from a source renowned for poor original processing (e.g. newspaper archives), it might be quite reasonable to reprocess large numbers of prints if one could know that the treatment was necessary and effective. (though, here also, the treatment of first priority must be control of the environment — lower humidity will decrease sulphiding of poorly processed prints as well as oxidation of all prints.)

To obtain some indication of the extent of residual chemistry in commercially processed prints and of the effectiveness of reprocessing in its removal, this author recently tested sixty silver-gelatine snapshots processed by photo-finishers, all dated and evenly divided among the 1920s, 1930s and 1940s. They were chosen to represent a range of materials, sources and conditions. All had clear margins on which the ST-1 and HT-2 tests were performed and evaluated. Each print was then cut into four strips which were given different treatments, and each strip was retested and evaluated. All washing was accomplished in a succession of room-temperature tap-water baths, gently agitated, with the prints throughly drained between baths, and the baths changed every 5 minutes for an hour.[22] This washing method was judged to be as vigorous as most older gelatine prints could withstand without damage. The fixing solution was a plain thiosulphate bath of 100g sodium thiosulphate (pentahydrate) per litre of solution, divided into two successive baths, thus supplying adequate fresh thiosulphate ion without great excess, and avoiding the difficulties of increased retention caused by low pH, and the additional complication of unnecessary hardeners. The washing aid (Kodak Hypo Clearing Agent) was used at the usual dilution, and the hypo-eliminating bath was the standard formula specified throughout the restoration literature.

Few of the prints showed the presence of residual silver: the prints were spotted with the ST-1 solution, allowed to sit for 2 minutes, blotted and then washed to remove water-soluble components of the stain, making it easier to judge the amount of insoluble silver sulphide formed. After drying, no silver sulphide stain at all could be seen on thirty-six of the prints in the sample; a barely perceptible stain was visible on seventeen; and seven showed obvious light yellow stains. When the positive-testing prints were re-fixed, hypo-cleared and washed and then tested again, no stain was formed. In this group of prints the presence of silver from the silver-thiosulphate complex was slight and could have caused significant staining on only seven prints. Judging from the amount of highlight stain already present in many of the prints, it is likely that the complex had already broken down fairly completely in most of them. Re-fixing was effective in removing the remaining residual silver complex.

In contrast, nearly all the prints showed significant amounts of residual thiosulphate to be present (90%) and some prints stained very deeply (patch No. 3 and higher on the Kodak Hypo Estimator). Strips of the prints were treated and retested: washing alone was very effective in reducing the response of prints to the test (bringing subsequent HT-2 tests to below No. 1 on the Hypo Estimator). Hypo-clearing followed by washing was about as effective as washing alone. Re-fixing, hypo-clearing and washing was slightly more effective than washing alone for most prints, but for some prints the stain was increased (i.e. new hypo had been introduced and retained). Re-fixing, hypo-clearing, hypo-eliminating and washing was consistently the most effective at reducing the stain level (though the actual difference in stains was slight), but hypo-elimination also bleached the image noticeably in highlight areas of many prints, and swelled the gelatine as well, promoting some frilling and physical damage. These results may provide some indication that re-fixing may be less necessary than

had been assumed, and washing more effective, though certainly the washing method employed is of great importance. This is only a small first step — much work is needed to fit the procedure to the needs of older prints, maximizing the benefits and minimizing the damages of the treatment, and to improve the testing methods, before reprocessing — the simplest of the silver treatments — can be recommended for use in collections.

The situation is similar or worse in regard to other, less studied, more complicated silver treatments. Just as the 'easily used' test solutions and the reprocessing procedure, typically covered in a mere sentence or two in the restoration literature as though they were unquestioned standard practice, become, on examination, vast abysses of uncertainty into which countless man-hours of research will have to be placed before they can be actually used, so, too, it is with the other silver treatments — bleaching and redevelopment, image intensification, etc. Here again, the restoration literature is, at best, naive, hopeful and uncritical; and whatever the intentions may have been, the result has been most misleading.

We would like to suggest that given the current state of photographic conservation, and the long pre-existence and slowly advancing nature of most of the deterioration processes, conservators direct their attention to improving the storage and handling conditions of photographic collections, to performing the practical research on specific conditions and treatments that conservators need to do themselves, and to prodding, demanding, encouraging and supporting basic research into the materials, which must be left to well-trained scientists working in well-equipped laboratories; and that until the combined research effort has yielded solid, reliable results, treatments be postponed and minimized as much as possible. Compared with analogous problems in paper conservation, the materials of photography are more fragile and sensitive, physically and chemically, and the delayed consequences of ill-advised treatment are more likely; less margin for error exists; and damages and repairs are usually more obvious — the materials are less forgiving, less easily manipulated, less amenable to treatment. In other fields of conservation a more complex technology has generally been needed to conserve the products of a less complex technology. Photographic prints are already the product of a highly complex technology and it is not surprising that it should require time and sophisticated, long-term scientific help to develop a technology to conserve them. What is unclear is from where and when such help may be forthcoming.

Notes and References

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22. Tap water was used here only for the sake of economy in an initial experiment. For treatment of prints, a cleaner, more controllable, water source is needed.

5.2

Library and Archival

5.2.1 Developing a conservation policy: The Harold B. Lee Library

Craig W. Jensen

For an institution to effectively deal with conservation problems, a detailed conservation policy needs to be written. This policy should be a comprehensive document mandated by the administration. In order to better utilize and preserve the collections, this detailed framework needs to include and deal with administrators, librarians, curators, archivists and patrons as well as the conservation staff. This paper deals with why a policy was needed at Brigham Young University's Lee Library, how it came about, some aspects of the policy's design and some examples of how it has been effective.

Despite growing interest in the conservation of library and archival materials, few institutions have satisfactorily dealt with the problems of their deteriorating collections. There are many reasons for this failure, the most common being a lack of adequate funding. Another major cause for failure is the lack of a comprehensive administrative framework within which to work. A library administration, even with the most stringent budget, could be much more effective in preventing deterioration of its collections with an effective conservation policy.

The Brigham Young University's Lee Library, like many other research libraries, has experienced very rapid growth and expansion in the years following World War II. The library's collection, numbering only 170 000 volumes in 1950, is now approaching the 2 million mark. The Special Collections have 160 000 rare volumes and 12 000 linear feet of manuscript and archival materials.

During this period of growth little attention has been paid to the conservation of these materials. Increasingly, however, knowledge of the instability of modern papers and the ever-increasing value of the library's holdings brought attention to the problems of conservation. Out of this growing awareness and along with the decision to participate in the Association for Research Libraries' Collection Analysis Project, the Lee Library administration decided to examine seriously the problems of conservation. From this experience the commitment to produce a responsible and systematic conservation programme has emerged.

It should be recognized, at the onset, that developing a conservation policy will require a significant commitment of time. To our knowledge, excepting a very good paper by Carolyn Clark Morrow entitled *A Conservation Policy Statement For Research Libraries*,[1] no working model exists in conservation literature to aid in developing a conservation policy. A good case can be made for employing the services of an experienced conservation administrator to aid in the task of developing, writing and implementing a policy. If, however, a practising conservator were to undertake such a project, long hours would be spent away from the work bench researching, writing and implementing such a policy.

The latter has been the case at the Lee Library and production in the conservation laboratory has been cut back considerably. However, the positive effects of the developing Lee Library Conservation Policy are beginning to be felt in the conservation process as a whole. Probably the most significant

benefit realized has been expanded and improved communication.

Of course, the conservation committee is the official forum for communication and discussion of conservation problems and needs. Committee membership should consist of permanent and rotating members. Those with permanent membership of the Lee Library Conservation Committee, such as the special collections librarian, the head archivist and the assistant director of the library for collection development and preservation, have an active concern with conservation matters. As conservator, the author was chairman of the conservation committee when he presented his paper to the Cambridge 1980 Conference. It is now felt that the chair is better served by a full-time administrator; so the Assistant Director of Collection Development and Preservation is now chairman, the conservator becoming a permanent advisor/member of the committee.

The rotating members of the committee represent the various sections of the library collection that circulate, the Lee Library having an open-stack arrangement. These members serve a one-year term. Because of the broad representation on the committee and the differing expertise of each member, the committee has been responsible for a significant portion of the research and writing that has gone into the conservation policy. The committee is also directly responsible for implementing a conservation education programme for staff and patrons, an important communication process in itself.

Conservation awareness, in the Lee Library staff, seems to be increasing, not only through participation on the conservation committee but through other personnel as well, working on developing the conservation policy. An example of this awareness and participation is seen in the development and organization of the *Emergency Preparedness Manual,* a section of the Lee Library Conservation policy.

This manual's existence has only been made possible through the direct involvement of several library and non-library personnel. Initial involvement included the library director. He listened to the proposal and gave the go-ahead. He further endorsed the manual's development by offering the finished document as a working model to other university libraries in the area.

The assistant director of the library for budget and administrative services was initially sceptical and uninformed concerning conservation policy and emergency preparedness in general. After presenting the initial research for the plan, not only was he more informed but he also agreed to make contacts with the University Physical Plant and Maintenance personnel. This assistance proved particularly helpful since the Preservation Department had been very critical of the air conditioning and heating engineers for failure to meet the established environmental standard.

The University Utilities engineer was very defensive, because of the friction just mentioned, and several meetings were held before this defensive attitude began to break down. The strategy used was not to attack but to ask for assistance and to involve the personnel from whom we needed cooperation and help in the process. This same utilities engineer, upon understanding the purpose for an emergency preparedness manual, even agreed to serve on the action team defined in the manual, and to be on call 24 hours a day in the event of an emergency. Also, by easing tension, more cooperation in the area of environmental controls is now being experienced in the library.

One final example of this type of increased goodwill concerns the assistant director of the library for Collection Development and Preservation. He felt too much time was being spent on the project. However, when the *Emergency Preparedness Manual* was completed and delivered to him for approval, he praised the effort as being thorough and complete and even offered to have it published.

Other administrators and staff members involved with development include the director of the University's Physical Plant, the head of custodial services, the chairman of the library's bibliographic department and Preservation Department staff members.

Non-university personnel have also become involved, including local fire fighters who will attend a training session on the nature of library materials and problems associated with water damage, to be conducted by the Preservation Department.

Outside contacts also include agreements for emergency use of an environmental chamber located at a nearby military installation, for freeze-drying water-damaged library materials.

Effective communication also aids in determining which materials in the library will be preserved and how and when they will be treated. For instance, through a series of interviews, discussions and exchange of ideas between the conservator and the Archives and Manuscripts curator, a priority listing of twenty-five important collections has been compiled indicating the need for preservation. This priorities listing was determined by evaluating curatorial information such as monetary value of the collections, amount of use, intrinsic value of the

material and the importance to the collection as a whole; as well as conservation information such as type and rate of the deterioration, date and origin of materials and ability of technical staff to perform the treatments needed.

All of these collections date from the mid-nineteenth to early twentieth centuries and are in badly deteriorated condition. They are also some of the most important papers in the collection. With this priorities listing more detailed surveys can now be undertaken, collection by collection, and preservation treatments can begin on a better organized and larger scale.

Improved communication has also aided in setting priorities for preservation in the Special Collections rare book section and priorities are in the process of being set for preservation of the open-stack circulating collections of the library.

The Priorities section of the Conservation Policy also includes priorities for staff time. For example, the conservator's time has been divided to include 20% for administrative responsibilities and 80% for technical work in the laboratory. This technical work time has been further divided, with one half for rare books and one half for manuscript and archival material. By establishing time divisions, efficiency is improved and larger projects can be undertaken, such as a large collection of early Morman letters, work on which was to have begun in October 1980.

Communication in the carrying out of priorities has been further facilitated by the use of conservation referral forms. One variation of this referral form is now being used in the processing of a large photographic collection. The collection includes everything from daguerreotypes to modern resin-coated prints. This referral form for photographic materials has been designed to include not only classification numbers but a checklist of symptoms of deterioration to be marked by archivists for future referral to the Preservation Department.

Similar forms are being designed for use by curators in reviewing the condition of flat paper, bound materials and some works of art on paper.

In the Archives and Manuscripts Department, an active programme of reviewing processed materials has begun and as conservation problems are discovered the referral forms are filled out. Also, as materials are taken from storage and presented to patrons for use, they are checked for problems and the referral forms are used to indicate those problems.

All of the aforementioned aspects of the Lee Library Conservation Policy have made an overwhelming difference in the potential of the Preservation Department. The policy can be seen as a guide to conservation for the library. With materials deteriorating at an alarming rate, by bringing together the expertise of conservator and curator, archivist and librarian, the mass of the library begins to take on form with regards to conservation. Through development of the Lee Library Conservation Policy, conservation has become a precise and calculated programme. The Preservation Department, instead of working piecemeal and by referral only, now works on entire collections, often grouping like work for more efficient use of space and facilities, and increasing output considerably.

By September 1980 The Lee Library Conservation Policy had been developing for more than a year — taxing work, and not finished yet. But, it seems worth the effort. The work of the Preservation Department is now visible. Whole collections are being preserved, with priority being given to the materials that are deteriorating the most rapidly.

Developing this policy has been not only time consuming and difficult but, on occasion, had nearly been abandoned because of conflict and disagreement. However, now that major portions are complete and the benefits are being realized, the Lee Library Conservation Policy is seen as an essential asset to effective library administration.

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5.2.2 The treatment of modern records in India

Yash Pal Kathpalia

The importance of thorough testing of materials and processes before their use in conservation is emphasized. A brief history of the development of the treatment of records in India is given, together with a description of the present-day housing conditions and conservation treatments currently in use in the National Archives.

An appendix lists the conservation, training, research and reprographic facilities of various archives in India.

Introduction

Preservation of archival materials is not mere application of paste and paper: it is much more than that. It involves scientific investigation and proper diagnosis of the damage based upon which information evaluated from tests; also the use of materials and processes which will help to preserve rather than contribute to their disintegration.

The paper of a document may appear to the naked eye to be in good condition. However, if tested, it may be found to be acidic. If such a document is not deacidified, it may not only itself become brittle during storage but also affect the other sheets or materials in contact with it. Acid migration can affect not only paper and ink, but, if the document forms part of a bound volume, the binding also may be affected.

There are instances in every archive where untested methods, improper storage and indiscriminate use of chemicals have been used on records resulting in untold damage.

Older techniques

For example, in India, Samuel Charles Hill, Officer-in-Charge of Records, took steps during the nineteenth century to rehabilitate the fragile papers in his custody. He introduced, at the recommendation of the India Office, a superior quality of tracing paper for the strengthening of brittle papers. With time, the tracing paper turned opaque with the result that writing below became illegible. Much difficulty has been encountered in the removal of this tracing paper prior to modern repairs. When detached it tends to remove the fibres of paper and thus the writing. It is evident that instead of paste a type of glue was used to reinforce the fragile sheet with tracing paper. Hill cannot be blamed for using this paper as he was guided by the expert opinion then available.

Another example of an improperly tested method occurs in the history of the US Library of Congress, which has given up lamination of documents completely. Laminated documents have become stiff, discoloured and even in some cases cracked, making the writing below illegible. It appears that this results from lamination being carried out without prior deacidification. However, if lamination had been affected after deacidification, then this would have been proof that too much alkalinity is harmful for document lamination. Unfortunately, the US Library of Congress has no record of what

preliminary treatment was carried out on these laminated documents.

Development facilities

In India the first step to introduce repairs with traditional materials such as Japanese tissue paper and silk chiffon, which have withstood the test of time, was taken in 1920 by Mr A. F. Scholfield, the first Keeper of Records of the then Imperial Records Department. His is the only instance of a Keeper of Records in India who repaired documents with his own hands. The last Keeper of Records and the first Director of Archives,[1] Dr S. N. Sen set up a small laboratory to develop newer techniques and find suitable substitute materials for preservation work. To him also goes the credit of recruiting a chemist to take charge of the Preservation Branch and to mechanize both the conservation and restoration work. A machine laminator (hydraulic — flat-bed type) and a vacuum fumigator were purchased from the USA after World War I, as was an air-cleaning unit.

Since then, facilities for preservation work, i.e. both for conservation and restoration, have increased manifoldly. Details of facilities available in the National Archives of India, New Delhi and other archival institutions in India are listed in the Appendix.

Modern methods

Some notable procedures have been developed in the National Archives of India with the help of its research laboratory. One process — solvent lamination — has established itself and is being used by an increasing number of countries. Fifty institutions in twenty-four countries use this process of restoration.

Besides records on paper, the National Archives of India has microfilms, photographs, maps and charts. There are no audio-visual or machine-readable records in the Archives.

Conservation

In the National Archives of India stress is laid on proper housing. All records are stored in a three floor stack area, each floor having a mezzanine at a height of 12 feet. The stack area is fitted with steel shelving and some of the shelves are adjustable. All shelving is supported on steel columns right from the ground floor to the top.

Documents are stored in acid-free file covers and then in document boxes or tied as bundles in between two pieces of five-ply board. The storage of boxes or bundles is horizontal. Some bundles as well as volumes are stored vertically. Microfilms are wound on plastic spools and kept in stainless steel boxes. Each box is sealed with a tape and then kept vertically in cabinets inside the air-conditioned stack area. Negative photographs are kept in acid-free folders made out of glassine paper and then kept in acid-free covers. Folders made from polyethylene and polypropylene have also been tried. Photographic prints are stored in flat albums.

Maps are stored in flat folders and placed inside cabinets. Big maps are sectioned prior to keeping them in folders. Some big maps are kept in rolled form. For such maps horizontal storage is preferred.

The entire stack area is free of insects, the menace of white ants and high humidity. The ground floor is fully air-conditioned. Environmental conditions conducive to conservation, i.e. temperature 22°± 2°C and relative humidity 50%±5%, are maintained throughout the year. There is a provision for air-washing.

On the first and second floors during summer, desert-coolers are used to counteract dryness and lower the temperature inside the area. This, coupled with air-circulators, helps to maintain uniform temperature and humidity inside the storage areas.

There is provision for both fire detection and fire fighting. For the former, smoke detectors and for the latter carbon-dioxide gas cylinders coupled with water under pressure are used. A water tank, which always remain full, is located just outside the building.

All incoming records are vacuum fumigated and air cleaned prior to storage inside the stack area. For fumigation, carboxide gas — a mixture of carbon dioxide (9 parts) and ethylene oxide (1 part) — is used. Facilities are available for fumigation with paradichlorobenzene for insect-infested records and thymol for fungus-infested records. A mixture of paradichlorobenzene and thymol has also been successfully used in the archive wing of the Nehru Memorial Library where the author has set up a modern conservation workshop.

All windows are fitted with metallic wire-mesh and the ones with glass also have curtains. Entry to the stack area is restricted. Records are moved on trolleys both inside and outside the stack area.

The storage capacity of the stack area is 25 km, which is being augmented by construction of an annexe. This annexe will be completely air conditioned and will have five floors. The storage capacity will approximately be doubled.

Restoration

Until 1951 dextrine paste was used in the National Archives of India as an adhesive for the reinforcement of fragile documents with tissue paper (Japanese) or silk chiffon. This paste was found to be acidic as it contained arsenious oxide which was added to it as an insect poison. The author was associated with the development of an alkaline paste and arsenious oxide has been replaced with barium carbonate. The use of this paste too has been given up since 1974, when carboxymethylcellulose was introduced as an adhesive. Now all traditional repairs with Japanese tissue paper and silk chiffon are carried out with this CMC paste.

Deacidification

Since 1956 all records are deacidified prior to repair either by the Barrow two-shot method of calcium hydroxide and calcium bicarbonate solutions or using magnesium bicarbonate solution. For labile inks deacidification is carried out with barium hydroxide (Baynes-Cope method) or with ammonia in a chamber having 85% relative humidity.

Restoration techniques

For restoration, traditional methods as well as modern, i.e. lamination, both solvent and machine, are being used. We do not have a leaf-casting machine. For lamination in India we have five machines, one flat-bed hydraulic and two Macino-Impex impregnators are with the Archives, one Macino-Impex impregnator with the National Library, Calcutta, and one Barrow laminator with the UP State Archives at Lucknow. All the State Archives have now started using solvent lamination for restoration purposes. This has been possible because of the National Archives programme of supplying the two imported materials cellulose acetate film and tissue paper to these institutions.

Testing work

As a result of testing and research in the laboratory of the National Archives, indigenous materials suitable for both conservation and restoration have been developed. The only items that we import, as stated earlier, are cellulose acetate film and tissue paper and in these too we will be self-sufficient in the near future.

Conclusion

No country in the world can spare money for restoring all its archival holdings. It is, therefore, essential to lay stress on conservation techniques. it is in view of this we find the ammonia deacidification process to be very useful. It helps to deacidify records in bundle form or volumes on a mass scale. This deacidification is for conservation and is akin to fumigation for conservation purposes and can be repeated as and when necessary. Instead of ammonia, dimethylamine can also be used. Care should, however, be taken to carry out such work where facilities for air extraction are available.

Appendix

The information about the various archives and institutions in India, listed in this Appendix, is arranged under the following headings:

Conservation facilities

(1) Steps taken for protection against damage by insects and insect infestation.
(2) Steps taken for protection against fungus infestation.
(3) Protective measures against the deteriorative action of light.
(4) Protective measures against the deteriorative action of heat.
(5) Protection against the adverse effect of moisture.
(6) Arrangements for fire-detection and fire extinguishing.
(7) Information about building.
(8) Shelving (type of) use.
(9) Methods used for storage of archival materials.

Training facilities

(1) Type of training provided by the institution itself.
(2) Number of technical staff.
(3) Training received by staff.

Testing facilities

Help given to others in conservation and restoration

Reprography

(1) Processes in use.
(2) Numbers of staff.
(3) Methods of storage.

Notes supplementing above information

National Archives of India, Janpath, New Delhi 11001, India

Conservation: (1) vacuum fumigation using ethylene oxide and carbon dioxide mixture (ethoxide), also fumigation with paradichlorobenzene and use of insecticidal spray; (2) fumigation with thymol, also spray of thymol solution (10%) in methylated spirit, use of fungicides (paranitrophenol); (3) curtains, use of boxes, switching on light in the storage area only when required; (4) and (5) air-conditioning, 24 hours temperature 22-25°C; RH 50-55% in one wing, in others proper air circulation; (6) carbon dioxide extinguishers (see note); (7) own, one wing centrally air conditioned, also localized air conditioning elsewhere; (8) steel shelving, both adjustable and fixed type; also steel cabinets, cupboards; (9) in acid-free pulpboard folders, and acid-free cardboard boxes, also folders tied between two pieces of five-ply board; horizontal and vertical depending upon the needs and condition of documents, volumes stored vertically, maps flat.

Restoration: (1) manual processes, dry cleaning, compressed air (air-cleaning unit) and washing; (2) aqueous, using calcium hydroxide and calcium bicarbonate solutions, and gaseous using ammonia; (3) traditional processes, also solvent lamination; (4) lamination with flat-bed press; temperature 130°-135°C, pressure 29-35 kg cm^2 (400-500 lb/in^2); duration, 3 minutes (see note); (5) repair of documents on paper (100%), seal repair, map repair, guarding, binding including rebinding, tooling and LP mixture application (see note); (7) varied, good to very bad.

Training: (1) in-service; Diploma Course, theory and practical, (1 year) and short-term practical training in conservation and restoration techniques; (2) sixty-four, including five chemists; (3) two trained aboard (see note), rest in-service training.

Testing: full facilities for testing, evaluation of materials and processes and also for research, facility for work with infra-red and ultraviolet.

Help Rendered: technical advice and training to institutions on various aspects of conservation and restoration of records (see note), inspection, formulation of standards, also help in restoring of records of national importance with individuals and institutions on payment basis.

Reprography: (1) microfilming, photography, photocopying; (2) 17, one-trained abroad; (3) metal cases, acid-free pulpboard cartons, temperature 22-25°C and RH 50-55%; stored in steel cabinets; vertical.

Note:
(1) palm leaf, birch bark and parchment documents are being repaired, also humidification and flattening is carried out.
(2) In the United Kingdom at the Public Record Office and the British Museum, London and in the United States of America at the US National Archives and the US National Bureau of Standards, Washington, D.C., New York Public Library, Hall of Records, Annapolis, Virginia State Archives and Illinois State Archives.
(3) Help rendered in setting up conservation laboratory and training both theoretical and practical to National Archives, Venezuela, and National Archives, Indonesia; to State Archives at Florence and Venice in Italy in salvaging flood-damaged records and to National Archives, Singapore, in planning their building; to National Center of Archives, Baghdad, Iraq for setting up conservation laboratory and also a building for its Archives.
(4) Staff from Nepal, Ceylon, Afghanistan, Burma, Singapore, Malaysia, Nigeria and Kenya received training at the National Archives, New Delhi.
(5) Cellulose acetate film and tissue paper are being imported from USA and UK, respectively.

State Archives, Rajasthan, General Records Building, Bikaner

Conservation: (1) spraying with insecticidal solution (chlorinated hydrocarbon), use of naphthalene; (2) fumigation with thymol; (3), (4) and (5) yes, but not specified; (6) fire extinguishers; (7) own, but not air conditioned; (8) steel shelving also cement shelving; (9) in folders and boxes also tied in cloth *(Bastas)* horizontal and vertical depending upon needs and condition of records.

Restoration: (1) manual cleaning and washing; (2) none; (3) traditional methods, also solvent lamination; (4) none; (5) repair of documents on paper, guarding, rebinding and binding also flattening of documents; (6) varied: brittle (20%), semi-brittle (30%) and good (50%).

Training: (1) yes, 15 days training in restoration; (2) nine, including a chemist; (3) two received training at National Archives, New Delhi.

Testing: none (see note).

Help rendered: advice on conservation problems and training.

Reprography: (1) microfilming, photocopying; (2) three; (3) film rolls packed in carton boxes, kept in steel cabinets and stored at room temperature.

Note:

(a) Preservation laboratory is being set up.

(b) Materials, training and technical advice are sought from National Archive, New Delhi.

Orissa State Archives, New Secretariat Building, Bhubaneswar-1

Conservation: (1) fumigation with paradichlorobenzene; (2) fumigation with thymol; (3) kept in boxes; (4) and (5) none except air circulation by means of fans; (6) extinguishers only; (7) own but not air conditioned; (8) steel shelving; (9) in folders and boxes; horizontal and vertical.

Restoration: (1) vacuum cleaners and washing; (2) none; (3) traditional process; also solvent lamination; (4) none; (5) repair of documents on paper, map repair, guarding and binding; (6) frail.

Training: (1) at National Archives, New Delhi, also in-service; (2) five; (3) trained at National Archives, New Delhi.

Testing: none.

Help rendered: advice on pest control and repair of records.

Reprography: (1) microfilming; (2) two; (3) under ordinary existing conditions for want of air conditioning and storage cabinets.

Note:

(1) Repair materials are procured through the National Archives, New Delhi.

Department of Archives, Elphinstone College Building, Bombay 400032

Conservation: (1) fumigation with paradichlorobenzene; (2) fumigation with thymol; (3) kept in boxes; (4) and (5) by air circulation only; (6) smoke detectors and fire extinguishers; (7) adapted for archive use, but not air conditioned; (8) steel shelving; (9) in boxes, horizontal.

Restoration: (1) manual cleaning and washing; (2) none; (3) traditional processes; (4) none; (5) repair of documents on paper, map repair, guarding and binding including rebinding; (6) good.

Training: (1) in-service; (2) six; (3) three trained locally.

Testing: none.

Help rendered: advisory only.

Reprography: none.

State Archives, Andhra Pradesh, Tarnaka, Hyderabad-7

Conservation: (1) use of naphthalene; (2) fumigation with thymol; (3) window panes are of green glass; (4) and (5) none except air circulation; (6) iron partitions in the repository, fire extinguishers; (7) own, not air conditioned; (8) steel shelving also steel almirahs; (9) tied in cloth *(Bastas),* also tied between two pieces of wooden boards, horizontal and vertical depending upon the condition of documents and records.

Restoration: (1) manual cleaning and washing; (2) none; (3) traditional processes; (4) none; (5) repair of documents on paper (90%), map repair (100%), seal repair, guarding, binding including rebinding, tooling and LP mixture application; (6) generally good.

Training: (1) in-service; (2) twenty-seven; (3) all trained locally (see note).

Testing: none.

Help rendered: advisory service, also training for staff of sister institutions within the region.

Reprography: (1) microfilming, photocopying; (2) two; (3) storage under normal conditions.

Note:

(a) Training received at National Archives, New Delhi.

(b) Seek help of National Archives, New Delhi, in all technical matters.

State Archives, Tamil Nadu, 6 Gandhi-Irwin Road, Egmore, Madras 600008

Conservation: (1) fumigation with paradichlorobenzene (see note); (2) fumigation with thymol; (3) precaution taken against direct sunlight falling on records by providing sun shades; (4) and (5) air circulation is maintained; (6) fire extinguishers and fire hydrants; (7) own, not air conditioned; (8) steel shelving also wooden shelving; (9) records tied into bundle shape between teakwood boards also kept in volume form, horizontal and vertical depending upon the type of documents and records.

Restoration: (1) vacuum cleaning and washing; (2) aqueous, using calcium hydroxide and calcium bicarbonate solutions; gaseous using ammonia; (3) traditional methods, also solvent lamination; (4) none (see note); (5) repair of documents on paper (100%), map repair, sizing, guarding, binding including rebinding and LP Mixture application; (6) satisfactory.

Training: (1) in-service training; (2) forty-six; (3) one trained at National Archives, New Delhi, rest in-service.

Testing: none.

Help rendered: advice on preservation of archives, also observation study and training to

sister institutions within the region.

Reprography: none.

Note:

(a) Lamination machine and vacuum fumigation chamber are being imported from USA.

(b) Materials obtained through National Archives, New Delhi.

Punjab State Archives, Baradari, Patiala, Punjab

Conservation: (1) fumigation with paradichlorobenzene, also use of an insecticidal solution containing DDT, naphthalene; (2), (3), (4) and (5) yes, but not detailed, except use of silica gel for moisture control; (6) fire-extinguishers; (7) own, but not air conditioned; (8) steel shelving; (9) tied in cloth *(Bastas)* and between teak boards, horizontal and vertical as needed.

Restoration: (1) washing in water and sand, also vacuum cleaning; (2) none; (3) traditional processes, also solvent lamination; (4) none; (5) repair of documents on paper (55%), and parchment (35%), also map repair, seal repair, guarding, binding, tooling, LP Mixture application; (6) 60% in deteriorated condition, rest 40% need minor repairs.

Training: (1) none; (2) two; (3) trained at National Archives, New Delhi.

Testing: none.

Help rendered: help in restoration.

Reprography: (1) microfilming, photostat; (2) and (3) not indicated.

Other Institutions in India having Conservation and Restoration facilities

Conservation Laboratory, National Library, Belvedere, Calcutta.
State Archives, Uttar Pradesh, B-44, Mahanager Extension, Lucknow-6.
Conservation Laboratory, National Museum, Janpath, New Delhi-110001.
Conservation Branch, Nehru Memorial Library, Teen Murti House, New Delhi-110011.
State Archives, Bihar, Old Secretariat Building, Patna-800015.
State Archives, Kerala, Fort, Trivandrum-23.
Assam State Record Branch, Shillong-1.

Other Institutions in India having few or no facilities

State Archives, Gujarat, Opposite M. J. Library, Elisbridge, Ahmedabad.
State Archives, Karnataka, Vidhana Soudha, Bangalore-1.
State Archives, West Bengal, 6 Bhawani Dutt Lane, Calcutta-700073.
State Archives, Harana, 67, Sector 11-A, Chandigarh.
State Archives, Delhi, 5-Alipur Road, Delhi-110006.

Note:

1. The Imperial Records Department was renamed the National Archives of India on 15 August 1947 when India became independent

5.2.3 Environmental control of modern records

James R. Briggs

Modern records comprise information in various inks, pencil, crayon, paint, etc., on papers of various types and other support material, data on magnetic tape, photographs on negative film or prints on a variety of materials, and a host of other items that come together in a modern records collection.

The implementation of environmental control is influenced by what materials are contained in the collection, their value and, undoubtedly, upon the funds available. The objective of this paper is to describe briefly from the point of view of a practising building services design engineer, various methods of controlling the environmental conditions at different levels of efficacy. The author would not claim particular experience of libraries or archives but rather of the general range of buildings, including factories, offices and hotels and a number of museums. The latter include an extension to the British Museum and the major new museum in Glasgow to house the Burrel Collection.

General considerations

The first need is to establish what conditions are required to be controlled. Those within the competence of the building services engineer are temperature, humidity, air quality and, to a slightly lesser extent, light. The control of these variables also affects condensation both upon surfaces and within material thicknesses and assists to avoid mould growth and similar deterioration and decay arising from water absorption and re-evaporation.

Temperature and humidity

These are related because, for a given absolute humidity (the actual quantity of moisture present) the relative humidity (the percentage of actual moisture present to that required to fully saturate the air) changes by some 4% for every 1°C of temperature change — because the quantity of water required to fully saturate the air rises as the temperature rises.

Clearly, it is for the conservator to say what is the ideal condition, and one definition has been given as providing pollutant-free air, total darkness, a constant temperature in the range of 15.5-20°C and a relative humidity constant in the range 50-60%. In addition, 'the structure should be vibration free with full protection against shock and soundwaves with an absence of all organisms (including humans), a site on high land, a fire proof structure, an elaborate emergency back-up system and the co-operation of the All Mighty'.

Conservators may not entirely agree with this but the author's experience is that everybody agrees that the relative humidity must be maintained as constant as possible while there is some disagreement as to the precise level and as to what the temperature should be.

For paper the ideal is that the moisture content is as when it was made and the environmental conditions such that water is neither absorbed by nor evaporated from the paper. Failure to achieve this leads to the edges of a pile of paper, or book, becoming swollen and waved if moisture is absorbed or tight edges and a baggy centre if water

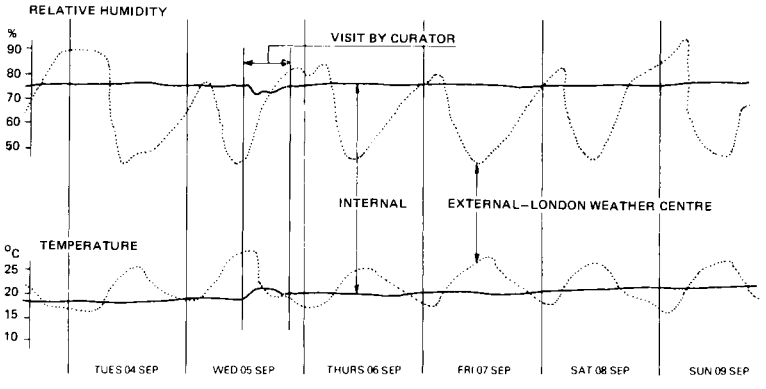
is lost. For modern papers a satisfactory condition is possibly 21°C at 40—50% RH, whereas old parchment and vellum need a higher moisture content and some 55—65% RH.

For paper with printing the effect of moisture on the ink also needs to be considered, since this can become an active acid and corrode its way through the page. Temperature is an important factor in this and it has been said that every 10°C rise of temperature halves the life of a book.

But the temperature selected will have to take into account the needs of people, who generally require a temperature of at least 18°C, and preferably 21°C, to be comfortable. If this is not provided human actions could well be more harmful than the higher temperature.

For the control of temperature and humidity it is important to take into account the 'response' of the building structure and contents. Figure 5.1 shows the variation of both internal and external temperatures and humidity for a week in the Royal College of Music Instrument Museum. This has a full air-conditioning system and at first glance the internal conditions seem to be satisfactorily constant, whereas the external variations are significant. In fact, the trace was taken with the air-conditioning plant shut down and the steady internal conditions were obtained simply by heat being absorbed and then released by the structure and contents. Note the small variation caused by a visit of the curator who affected the balance by switching on the lights.

Figure 5.1. Internal and external temperature and relative humidity recordings, Royal College of Music Instrument Museum, London



Air quality

This means the degree to which pollutant gases, vapours and particles that are present can be controlled by replacing the internal air with outside air at a sufficient rate, if the outside air quality is good enough, or by passing the air through air filters of an appropriate standard, and generally requires a mechanical ventilation system of fans and air ducts.

The best standard as to what the conditions should be is that given by Garry Thomson, Chief Scientific Officer of the National Gallery of London. This is that the maximum permissible internal concentration of sulphur dioxide should not exceed 10 micrograms in one cubic metre of air — which is the sort of level found in the countryside far from any industrial process. This is just one of the pollutant gases, albeit probably the most destructive.

For particles, the best reference is that of *BS 5295* Part 1 1976, which gives, for 'clean environments', meaning a laboratory, the particle count should not exceed 3000 particles in one cubic metre of air of size 0.5μ to 5 μ with no particles larger than 5μ.

These standards are probably rather better than essential for most things but possibly are required for sensitive items such as photographic film.

Light

Light is important to the building services engineer because it is an energy transmission that turns into heat when it is absorbed at a surface. This produces a rise of surface temperature and consequent reduction of relative humidity. Artificial electric light does not transmit energy to the degree required to cause a troublesome temperature rise on a surface, unless it is very directional in nature, such as a photographer's light. Natural lighting by glazing is a source of problems and the total amount of energy that enters through glass can be very

substantial and cause a general air-temperature rise and reduction of relative humidity.

The photochemical effects of light are outside the scope of this paper but, of course, can be quite as damaging as the effects of heat.

Methods of control

Temperature by heating

Temperature may be controlled to be *not less* than a given value by *heating* and the efficacy of control in a space will depend on both the accuracy of the sensor (usually a thermostat) *and* the adequacy of the circulation of heat within the space.

Most forms of heater — radiators, convectors (natural and fan types), radiant panels, etc. — are reasonably effective in distributing heat, because, for all, a considerable proportion of their output is by convection. Heaters in several positions are clearly better than a single heat source.

Heaters with a large radiant output should be avoided for conservation because they will raise local surface temperatures, leading to a local relative humidity lower than that of the space average. Hence the best form of heater for conservation is one having only convective heat output and the best of this category must be heater batteries in a mechanical ventilation system in which the air, and thus the heat, is positively distributed.

In order of merit therefore, the forms of heating are:

(1) Mechanical ventilation system heater.
(2) Built-in fan convector.
(3) Built-in natural convector.
(4) Cased fan convector.
(5) Cased natural convector.
(6) Radiator.
(7) Radiant panel.
(8) Radiant unit.

The radiant unit could be either direct electricity or gas and all the others could also be direct electricity, gas or oil but more usually would be piped hot water which is easier to control.

The temperature-control sensors provided with or built into the unit are usually less accurate than separately purchased sensors, probably because of the heat gain to the sensor from the unit. Care is needed to locate sensors so that they are not directly affected by either the unit or any other source of heat, such as the distribution pipes.

It should be noted that *heating alone* will result in *low relative humidities* in winter.

Temperature by cooling

To control temperature to a given value requires cooling in addition to heating. The control is similar to heating with the added complication that supply air streams set for correct air distribution with heating can be wrong for cooling — because a hot air stream will tend to rise and a cold to fall.

Cooling is usually only available by a convective source because exposed cold surfaces would attract condensation and soon become a problem. The forms available in order of merit are:

(1) Mechanical ventilation system cooler.
(2) Room air conditioner piped to external condenser.
(3) Room conditioner on external wall.

There are quite a few variants of the room air conditioner piped to an external condenser and the best types will be those capable of supply to an air duct distribution system within the space.

The same comments as for heating apply to cooling temperature control sensors. Normally the same sensor with changeover device is used as to control the heating.

Humidity control by the addition of moisture

In winter the external air moisture content is often well below that which is desirable and the methods of adding moisture in order of merit are:

For use with a mechanical ventilation system:

(1) Steam injection from purpose-made unit.
(2) Spinning disc unit.
(3) Fabric evaporator.
(4) Spray washer.

All, except possibly the steam-injection unit, must have a supply of water from which all solids have been removed — that is 'de-ionized'.

For use locally in a room:

(1) Heated pan evaporator.
(2) Spinning disc.
(3) Fabric evaporator.

Again a supply of de-ionized water is essential if the units are to be effective for any period.

The efficacy of the humidifiers depends on the same factors as those for heaters because moisture is distributed by air circulation. Its natural diffusion rate through the air is negligible. Clearly, therefore, a humidifier as part of a mechanical ventilation system is to be preferred.

Humidity control by the removal of moisture

In summer the external air moisture content is often well above that which is desirable and this adds to the moisture exhaled by people in internal spaces.

While there are local room dehumidifiers that do not require mechanical refrigeration, we doubt they could be used on any large scale. Normally the removal of moisture is only possible with mechanical refrigeration, that is, in a full air-conditioning system.

Air quality control

It is possible to install a variety of local room air cleaners but to obtain standards approaching those previously mentioned, only a filtration system in a central air plant is likely to be effective.

Light control

The ideal form of light control, meaning control of solar radiation, is to avoid windows. If windows are essential, they should be at least double glazed and equipped with an external shading device to reduce the heat gains into the space to the least possible.

Type of control

Clearly, for ideal conservation the only form of control likely to give fully satisfactory results is a mechanical ventilation system with air filtration, heating, cooling and humidification. Unfortunately, this is also the most expensive solution both in installation and running costs.

At a lesser provision than this there is a very wide choice but, in *Figure 5.2*, we attempt to show a comparison between the two extremes with three somewhere in the middle.

The figures can only be the most approximate guide as a lot will depend on the conditions required and the building configuration, but should be sufficient to decide which systems to investigate in detail.

The sytems range from full air conditioning on one side to local heating with humidistat override on the other. The installation costs, which are probably underpriced for the larger systems, are given in the first row of figures with an estimate of the approximate energy consumption and the average annual total effective cost on the bottom row of figures in the middle panel. The annual total effective cost is the energy plus the maintenance and operational costs plus amortization of the installation cost. Beneath that an attempt is made to show the percentage efficacy of the system as to temperature, relative humidity and air quality and also the percentage period of the year, very approximately indeed, over which the control is provided.

The full air-conditioning system is able to give control of all three parameters for all of the year whereas, with a ventilation-only system, that is without mechanical cooling, it is only possible to provide temperature and relative humidity control for half of the year.

Local conditioners and humidifiers are not so effective for temperature and relative humidity and have almost no effect on air quality. Local filters possibly could be provided, but these would be of a very low standard and it is doubtful if they are worthwhile. Central heating and local humidifiers are not as good as a mechanical ventilation system in the control of temperature and relative humidity because the heating undoubtedly contains some radiant component, and it is the air temperature that one is trying to keep constant to obtain control of relative humidity. Again, there is no possibility of air quality control.

The last system indicated has a much lower efficacy but it also has a very much lower cost. An example of such a system is an ordinary electric fan heater with a humidistat which opens and switches the heater off if the relative humidity drops below the setting. This has been tried out at Claydon House in Buckinghamshire. Whether this solution would be entirely acceptable for people is somewhat debatable, but it certainly takes the chill off, and perhaps people have got to get used to working in conditions where their clothing provides rather more of their personal environmental control than it does at the moment.

The system needed for a modern records collection will depend on the requirements of the collection and the heat gains and losses that are involved.

Full air-conditioning system

In a full air-conditioning system a fan drives air into the conditioned space and an extract fan withdraws air from that space and either discharges it to the atmosphere or recirculates it back with a proportion of fresh air to the supply fan after passing over the filter, the heater, the cooler and the humidifier. Thus the condition of the air is controlled in respect of temperature, humidity and purity.

SYSTEM	Full ducted air system, heating, cooling, humidifying, filtering	Full ducted air system, heating, — humidifying, filtering[1]	Local air conditioners and humidifiers[2]	Central heating and local humidifiers	Local heaters with humidistat override
COSTS £/M^2					
Installation	100	80	60	40	20
Energy Annum	10	8	12	4	3
Annual total	25	20	21	10	6
	%E %Y	%E %Y	%E %Y	%E %Y	%E %Y
EFFECT					
Temperature	100 100	100 50	90 100	90 50	70 50
Relative humidity	100 100	100 50	70 100	80 50	60 50
Air quality	100 100	100 100	0 0	0 0	0 0

%E = % Effective
%Y = % Year control obtained

Notes: [1]Could add cooling later [2]Possibly could have some token filtering

Figure 5.2. Type of system and control obtained. (Approximate costs as per 1980).

The fans, heater, cooler and filter with ancillary equipment are generally made up into a 'packaged' air handling plant as shown in *Figure 5.3*.

The air plant could be located on the roof or in the basement, as shown. Pipe connections may be very much more evident in the basement where they do not need weather protection and the basement plant can therefore be smaller than the roof plant which needs to incorporate the pipes and connections.

Whatever the type, the fundamental construction is a steel box with outer panels which need to be galvanized and made weather-proof if they are to be external and in any event thermally insulated.

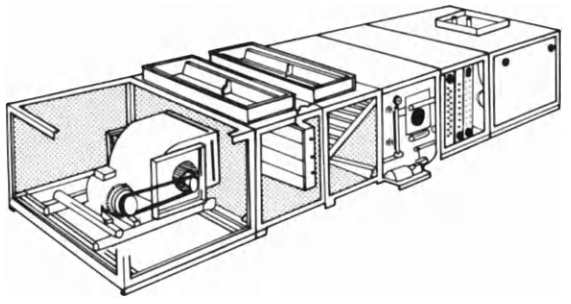


Figure 5.3. Air plant (Trane Climate Changer).

The largest component of an air-handling unit is often the fan, but in library installations the filter system can often be rather larger. A bag filter is often used because it has a high efficiency and is also able to take out the 'rocks' of air filtration. This is because its material is in two layers — an inner coarse layer and an outer fine layer. In built-up areas this may not be sufficient to remove all of the contaminants, in which case an active carbon or other 'absolute' filter would also be needed.

A cheaper filtration system which takes up much less space is the throw-away type.

The other main component of an air-handling unit is the device to change temperature either to make it hotter with hot water or steam or to make it cooler using chilled water. This is the 'coil' or 'battery' which is like a car radiator but rather larger.

Of course, this is just the air plant and there also has to be plant to generate heating and cooling. For heating it could be an oil- or gas-fired boiler plant or the heating could be done electrically. For cooling there needs to be some refrigeration system which, on the larger projects, takes the form of quite large compressors which need to be located in a basement with heat rejection equipment such as cooling towers on the roof.

Before moving on there are some do's and don'ts in connection with air plants.

For the components the filters should not include an electrostatic air cleaner because, although these are very effective in removing particles, they also produce ozone and nitrogen dioxide which can form nitric acid. Further, any particle that does get through has an electrical charge which can cause it to adhere to objects.

For humidification any form of evaporative system has its disadvantages. There are quite a few different types of evaporative humidifier. It can be a simple water spray, a wet pad which is saturated with water through which the fan blows the main air stream and the like. In all of these, maintenance has to be very thorough and regular if there is to be any chance at all of controlling microbiological growth and, if this is not successful, spores can be carried into the library area with unfortunate results. In addition, the deposits left when water evaporates can be left inside the air plant, which is not a happy state of affairs either.

The best form of humidification yet devised is that of the steam-generator humidifier, which does not have the microbiological problems although it does need water treatment if it is not to scale up very rapidly. One final warning on this is that the main building steam supply, if there is one, is not a satisfactory substitute for an individual steam-generator type. The former was used at the Royal College of Music with no less than five safety devices to prevent raw steam being blown straight into the Museum, but on several occasions all five devices failed.

Possibly the most important aspect of an air-handling plant is its location. Ideally, it should be in the centre of the conditioned space with direct connections to outside air for both supply of fresh air and discharge back into the air at different points so that there is no short circuiting. In this way long and expensive duct runs are not required. Clearly, however, the ideal cannot be achieved even if it were to be realistic. None the less we hope that we have stressed the point that long duct runs should be avoided wherever possible, and the best location will depend on the location of the space to be conditioned. A roof air plant has the advantage that there is no duct work to connect the plant to the outside air and that valuable floor space is not taken up either at the occupied levels or in the basement, but it does need to very carefully weatherproofed and streamlined and, although modern plant of reasonably high quality is now available, there are obvious maintenance objections.

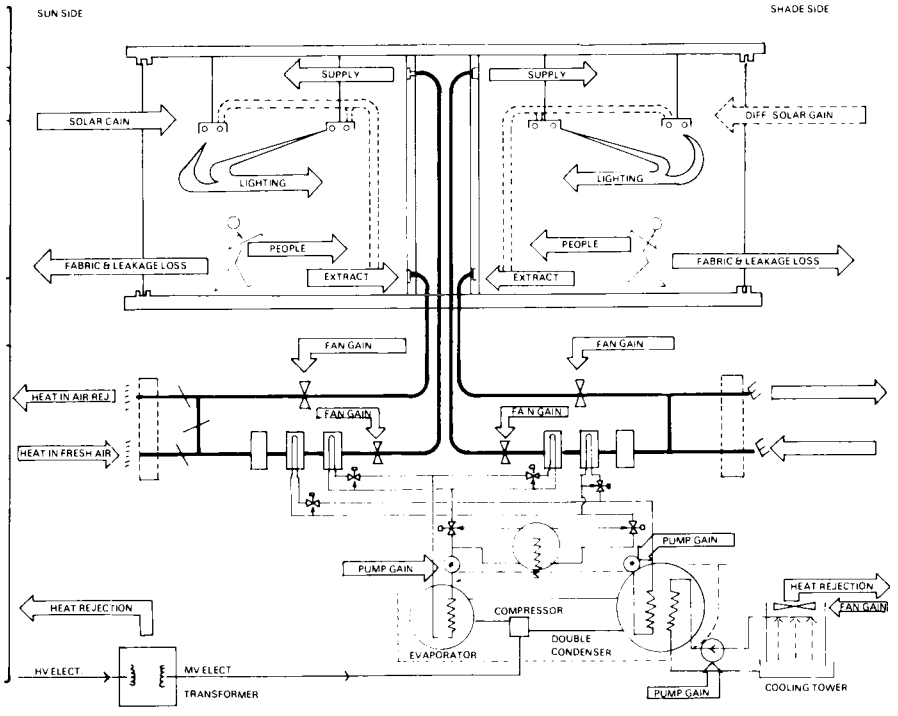


Figure 5.4. Heating and loss gains from a space.

Air-conditioning capacity

The temperature of a space depends on the rate of heat transfer inside to outside or vice versa plus the rate at which heat is generated within the space. Indication of these processes is shown on *Figure 5.4.*

To quantify the heat gains and losses is not easy in a space in which nearly everything is variable. The people come and go and are not the only variable; the lighting for one use could be quite different to that for another and the heat gains and losses from and to outside are clearly dependent on the external condition.

Heating and cooling loads in some detail are shown on *Figure 5.5.*

Note that figures have been given for the least and greatest situations that were foreseen and the mean of these two has in fact been taken as the design parameter. It would be unrealistic to design for the absolute greatest possible number of people, lighting loads, solar gains, etc., all occurring simultaneously.

Item		Simultaneous Demand kW			Consumption		MWh
		Least	Mean	Greatest	Least	Mean	Greatest
1 Space heating	HW	586	520	453	1781	973	164
2 Hot water	HA	25	38	50	35	176	317
3 Air reheat	HS	8	32	55	16	76	136
4 Heat distribution	HW	29	26	23	102	74	45
5.1 Catering	HA	21	65	109	37	131	225
Sub total 1		669	681	690	1971	1430	887
5.2 Catering, elec.	EA	6	14	22	15	36	57
6 Cooling	CS	111	243	374	244	489	733
7 Lighting	EA	120	242	364	368	1070	1773
8 Fans	EA	210	247	284	920	1704	2488
9 Cooling dist.	CS	22	35	47	43	104	164
10 Pumps etc.	EA	80	108	135	260	511	761
Sub total 2		549	889	1226	1850	3914	5976
Total		1218	1570	1916	3821	5344	6863
Concurrent Maximum Demand							
Winter (W)		615	546	476			
Summer (S)		141	310	476			
Always (A)		462	714	964			
That is, overall:							
Winter (W + A)		1077	1260	1440			
Summer (S + A)		603	1024	1440			
BEEP			1025			3797	

Figure 5.5.

Looking at the consumption figures, it is interesting to note that by far the biggest consumer of energy are the fans to drive the air around the building, 1700 MWh per annum at a cost of perhaps £30 per megawatt hour. The next largest consumer is the lighting and heating and cooling, which are not such large consumers, as you might imagine.

These figures are for the Burrell Museum in Glasgow, an artist's impression of which is given in *Figure 5.6*, and *Figure 5.7* a vertical view down onto the model showing the plan.

The other major item that has an effect on the conditions inside a space is the amount of glazing. Traditionally, galleries are provided with generous top day lighting which may well produce satisfactory conditions for viewing in certain situations but can be disastrous for temperature control, when the solar energy turns into heat once it has got through the glass.

The ideal solution is not to have windows. But where there are a lot of windows, as in the Burrell Museum, the solution must be to provide some solar shading. These should be external if they are to have the greatest effect, but solar blinds are expensive both to install and subsequently maintain.

Internal blinds and sun shades can reduce direct radiant effects but heat will get into the building by passing through the glass and, although some of it radiates back out due to the high-temperature zone between the glass and blinds, the bulk has to be removed by the air-conditioning system.

A compromise solution is perhaps internal blinds underneath sloped roof glazing with a sealed glass laylight beneath, thus creating a void which can be mechanically ventilated to remove most of the heat before it actually gets into the space. The amount of air required, however, is quite large if the temperature in the void thus created is not to be impossibly high.

The moral is to avoid glazing, but, if you must have it, at least have double glazing and, preferably, triple glazing.

Minimal control system

If the control of humidity to not less than a given value is all that is needed, then a minimal system could be as *Figure 5.8.* In this, heat is supplied as required by the heater thermostat *except* when this would cause an unacceptable reduction of relative humidity.

The risk is that the room temperature will be inadequate but test results look promising — as *Figure 5.9.*

Energy conservation

The cost of energy continues to rise and is likely to do so for the immediate future, though we do not share the view that energy is on the way out. There seems to be a very large energy source shining on us every day and there cannot be a long-term energy problem. Nevertheless, the economics of the situation are such that for the next decade at least every care should be taken to limit the energy consumption to the minimum.

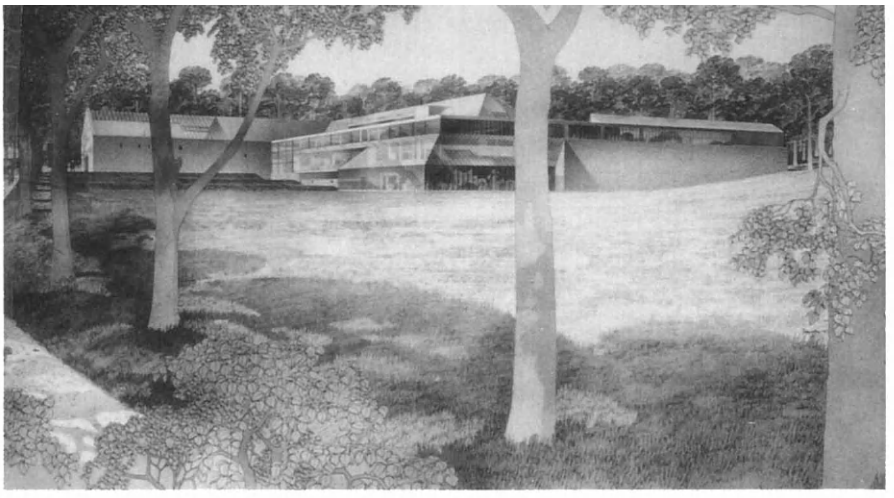


Figure 5.6. Burrell Museum, Glasgow. Artist's impression.

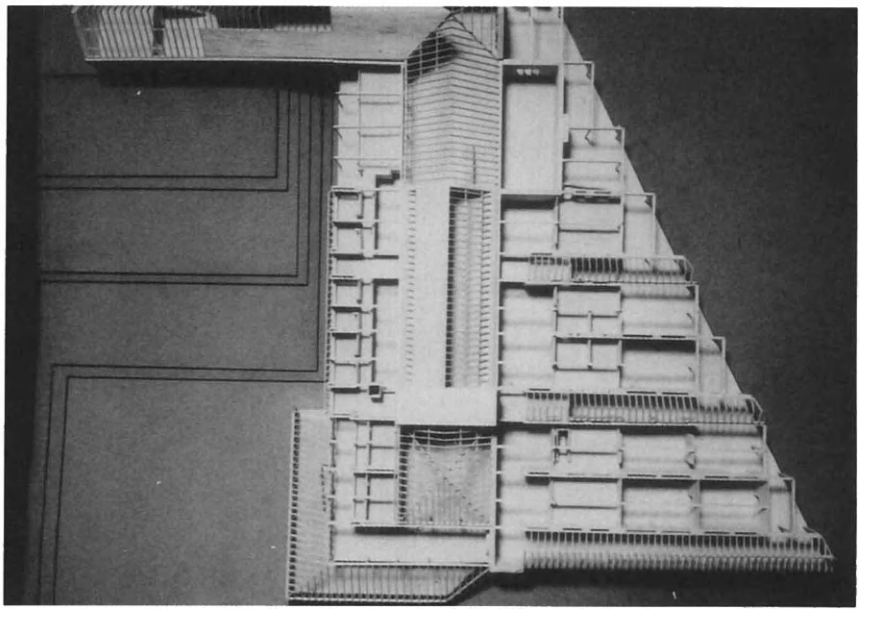


Figure 5.7. Burrell Museum, Glasgow. Model (plan view).

Some factors to reduce energy consumption should be mentioned:

Only install air conditioning for areas that really justify it. This can just be for the collection but, where there are a lot of people and no means of natural ventilation, it could be justified for people alone.

Free cooling: by this term we mean using the outside air to cool when it is at a sufficiently low temperature. The disadvantage of this in conservation terms is that the air only passes through the filter once before it gets into the conditioned space and is therefore held not to be clean as air that is continuously recirculated. While this may be true the energy savings can be quite large and we estimate that free cooling could contribute as much as 30 - 50% of the total refrigeration consumption. Unfortunately, it would not have the effect of reducing the size of the plant itself, only the number of hours that it would need to run.

Air leakage infiltration should be arranged to be the absolute minimum. Free cooling is fine when it is required, but when it comes in when it is not required, that is unfortunate. Air infiltration not only increases the heating in the winter and the cooling in the summer, but in temperature-control terms also imposes a load on the refrigeration plant to remove excess moisture in summer and on the humidification system to provide additional moisture in winter.

To quote a few figures, a one air change rate on a room of 7200 m^3 requires an additional heating of 40 kW and humidification of 13 kW to provide 18 litres per hour (4 gallons per hour) of water. The additional energy cost if all electric would be of the order of £30/$38 a day (1980).

Thermal insulation — modern standards of a 'U' value of .6 W/m^2 per centigrade mean that the heat loss through the fabric is relatively minor compared to the heat loss by air infiltration, but where the building is existing and the 'U' values are very much greater than required by current regulations, consideration should be given to improving the 'U' values. This can be achieved by adding thermal insulation with care that one does not create an interstitial condensation problem, which is particularly difficult in rooms which have high internal vapour pressure. This means that the ideal location for the thermal insulation is on the outside of the building.

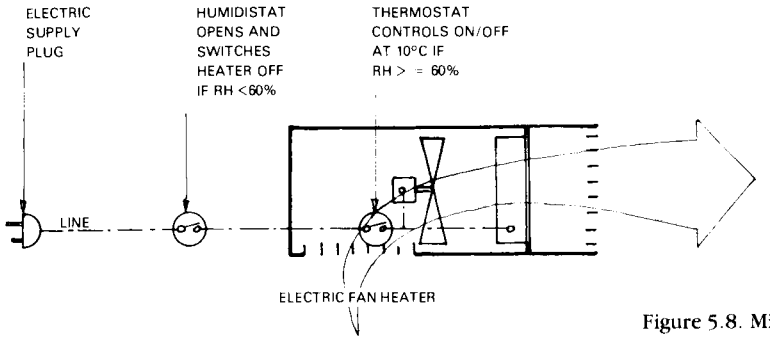


Figure 5.8. Minimum humidity control with heating.

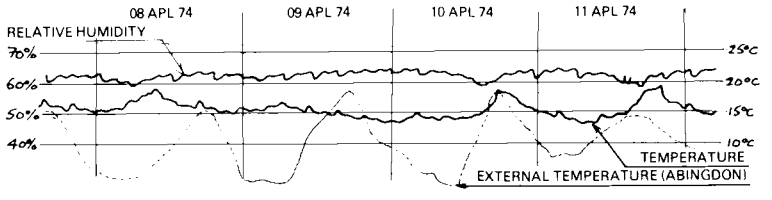


Figure 5.9. Temperature/humidity traces — minimum humidity control with heating.

Operation and maintenance

In conclusion we would mention that all the systems in the world are absolutely useless unless they are properly operated and maintained.

First of all the design must ensure that all components of the installation are readily accessible and the project documentation should give a clear and concise description of the installation together with fully documented and cross-referenced data about each of the components.

This sounds to be a very obvious requirement, but it is very difficult to achieve, and the building industry as a whole is very poor at providing adequate documentation. In recent years organizations have grown up specializing in planned maintenance, and consideration should be given to the appointment of one of these .

Probably, however, there is no real substitute for having on strength a fully and reasonably qualified engineer who is able to get to know the installation and to do all routine adjustments so as to keep it at optimum efficiency and efficacy.

Maintenance, however, is a subject that does need a lot more research and development outside the scope of this paper.

6.1. Paper deacidification in practice: topical problems

Margaret Hey

Introduction

During the Cambridge 1980 International Conference on the Conservation of Library and Archive Materials and the Graphic Arts informal discussion meetings were organized to support the formal lecture sessions. These allowed a venue for further comments and criticism and for the airing of other related matters of topical importance. The present article by a participant (and chairwoman of one of the meetings) delineates the main points of the discussions concerning the deacidification of paper together with personal observations on the three formal lecture presentations in the session devoted to alkaline buffering of paper. Reference is also made to publications consulted by the present writer since the preparation of her 1979 article, 'The washing and aqueous deacidification of paper[1]'. Together, these lectures, discussions and literature help to demonstrate the present state of awareness of information on paper deacidification some 50 years after the need for it was first put forward[2]. The outlook is not very encouraging, not so much because the information is unavailable, but more because it has not been assimilated well into working practice and into the general approach to the subject.

Alkaline buffering of paper: observations on formal conference presentations

The following brief observations arose from the formal conference lecture sessions and associated preprint articles. The first of these, by Vincent Daniels, concerned the aqueous deacidification of paper.

Daniels rightly made the point that water washing of paper will remove only soluble acidity present. However, he expresses some doubt as to whether cellulose acidity as such could contribute to paper deterioration (see section 2.3.1, p.110). Nevertheless, findings in 1951 and subsequently[2,3] appear to indicate that such acidity could indeed lead to the autohydrolysis (breakdown) of cellulose chains. It is also not possible to remove acidity due to the presence of alum by water washing[4]. These are both important factors to bear in mind when taking a decision on whether to deacidify or only wash (without subsequent deacidification) (see below).

It should also be noted that the Barrow two-stage deacidification process was devised as a means of rapidly lowering pH by immediate conversion of calcium hydroxide into calcium carbonate, and that its use *does not lead to higher precipitation of carbonate within the paper structure* — rather the reverse. Immersion in the very weak solution of calcium bicarbonate, which is all that can be prepared, washes away some of the calcium hydroxide solution from the paper, so leaving a rather lower final deposit of carbonate. If rapid conversion to carbonate is required, then the best way of accomplishing this in practice is to hang the papers in a fume cupboard, and arrange either a slow leak from a CO_2 cylinder (lead a tube to above the papers) or to put a dish containing solid carbon dioxide on a shelf above the level of the treated papers. Carbon dioxide is a heavier-than-air gas so

that it must be allowed to sink down over the papers. Normally, however, any conservation workshop occupied by several people will have air with a sufficient carbon dioxide concentration due to exhalation to convert the deacidifying agent in single leaves fairly rapidly.

Doubts were expressed by Hey[5] about the effectiveness of localized deposits of calcium carbonate. Ten years later she prefers the Wilson idea[6] that the function of the calcium ion primarily is to stablize the cellulose rather than, as calcium carbonate, to 'mop up' aerial acidity — important as that may seem. This point of view would appear to concur with Arney's findings that the presence of calcium carbonate appears to slow down cellulose oxidation.

Daniels states that barium hydroxide could be used in water, but this statement needs some qualification in that in water solutions barium hydroxide carbonates so rapidly that the solution rapidly become opaque with barium carbonate. The latter chemical is insoluble in water and totally ineffective as a paper deacidificant with no penetration into the paper structure. Barium hydroxide in water therefore becomes unusable within minutes of preparation.

It was mentioned that sodium bicarbonate or sodium sequicarbonate in the form of natron has been shown to have preserved ancient Egyptian linen bandages in a remarkably fresh state. However, it appears that such preservation was only possible because these textiles were in very dry environmental conditions — witness the sad decay of Bristol City Museum's Egyptian mummy after one hot, *humid* summer.

The Russian work in extending the list of alkaline buffers for paper deacidification referred to by Daniels was, unfortunately, all carried out using dry conditions only for ageing, and with negligible alkaline reserves. Had humid conditions been employed the defects associated with water-soluble alkali salts and hinted at by Daniels would rapidly have made themselves evident.

The point of view expressed that ageing tests are unreliable and 'can lead us to false conclusions' needs some qualification. They are so only if dry conditions alone are employed and if no attention is paid to the state of collections in different environments. It is unfortunate that the standard method presently available stipulates dry conditions and can be potentially misleading as to the actual state of affairs concerning the ageing procedures used by many researchers. For some 30 years now almost everyone working in this field has been critical of the applicability of the standard method in the conservation context, and often dry ageing as been supplemented with humid ageing conditions of the researcher's own devising. Accelerated ageing tests should not be carried out in a mental vacuum. Instead it should be borne in mind that storage in and exposure to natural environmental conditions always involves humidity to a greater or lesser extent, that water is the great destroyer of everything and that collections in humid climates are always worse off than those kept under more temperate conditions. Until the new ISO standard stipulating ageing under humid conditions is finalized, the present writer strongly recommends that all accelerated ageing testing be carried out using both dry and humid conditions. In this way the extremely damaging effects of moisture will clearly be seen.

In connection with Kelly's paper on 'Non-aqueous deacidification' it should perhaps be emphasized that, as there are no fundamental differences between the deacidification of paper on a mass or individual scale, the requirements which have been stipulated for the latter must be applied equally stringently to the methods suggested for the former. These requirements are particularly linked to the findings that calcium, magnesium and barium ions are the most satisfactory form of stabilization, that supression of catalytic metal activity is an essential side effect on deacidification and that deposition of an alkaline reserve at the time of treatment is fundamentally important if repeated treatments are not to be routine. These three requirements have been much stressed by the Preservation Office of the Library of Congress over the past ten years.

When evaluating any new method it is necessary to see how far it conforms with these prerequisites. If it falls down on any one it then becomes necessary to explain why this is being ignored. In a number of attempts to develop viable methods of gaseous or vapour-phase deacidification these basic requirements have not been vigorously applied, with the waste of much time, effort and money. It should be underlined that treatment with ammonia gas for alleged deacidification processes is totally different from treatment with liquid ammonia as proposed by Koura and Krause (see their article, 'Increase of paper permanence by treatment with liquid ammonia or ammonia solutions: Part 1. Fundamental basis and influence on fibre and paper structure and properties', section 2.1.3 above). Liquid ammonia has completely different properties from either ammonia gas or ammonia gas dissolved in water. Only the liquid ammonia has the ability to swell cellulose fibres and so re-form the paper's structure. This leads to the shrinkage of the paper area, and further research needs to be done on the

effect on the paper's image after treatment. A recent suggestion that paper be treated with 25% sodium hydroxide in order to swell its fibre structure, leading, so it is said, to reformation and greater strength, leaves the writer wordless with horror.

Of the gaseous methods of paper deacidification described in Kelly's paper, neither the use of ammonia gas nor morpholine vapour meets the essential requirements listed above. Any procedure needing repeated application simply is not acceptable, given the quantity of material requiring urgent treatment.

Kelly gave a fairly detailed description of the Library of Congress's own mass-deacidification technique which deposits zinc oxide in the paper. It was rightly pointed out that this compound degrades cellulose extremely rapidly in the presence of light and conversion to zinc carbonate now forms part of the treatment. However, to date no details have appeared to demonstrate that every treatment produces 100% conversion. Testing by effervescence with acid is a qualitative test, not quantitative. It is also necessary to know that suppression of heavy metal degradation also occurs (particularly important because of the high heavy metal concentration in nineteenth and twentieth century papers). A final point is that the aluminium derivative said by Kelly to be the new stabilizer for diethyl zinc must be shown not to be deposited in the paper treated. Although favourable comments on all these points have appeared in reports to various conferences, no professional publications have yet appeared at the time this article was prepared. Judgement on the long-term value of the Library of Congress's mass-deacidification technique must therefore still be suspended.

Concerning the method of deacidification presented by Smith in his paper, 'Mass deacidification' this liquid method is chemically very acceptable. The chemical employed, magnesium methoxide, does give excellent results which easily meet the three requirements given above, *provided* the paper be totally treated leaving no 'missed areas'. The method's big handicap would appear to be the need to sort out items carrying certain vulnerable modern inks. It is to be hoped that further developments will overcome these handling problems.

Conference Discussions

Colour changes due to deacidification

A discussion was arranged to deal primarily with actual or potential colour changes due to deacidification. Some examples of artifacts exhibiting such changes were provided by Milner, Keyes, Santucci and Waters. However, during this discussion it became painfully clear that it is simply not known with any degree of exactitude what is being treated in the majority of cases of colour change. The major reference book on historical dyes and pigments stops at 1835[9] before many of the most vulnerable modern pigments, dyes and inks came onto the market. Even if it was known what was commercially available at the time of production of the artifact concerned it would not always be possible to judge what was actually used in individual examples as very few systematic analyses have been undertaken in this field. This applies not only to watercolours, etc. but also to nineteenth and twentieth century inks (such as used in manuscripts, engravings, posters, etc.) Any institution blessed with both staff and money and willing to undertake systematic research in this area would earn the gratitude of all. But even with such an outline of possibilities often it still would be extremely difficult to know precisely which pigments, dyes or inks are present in any particular item — and hence the potential for colour change during or following deacidification.

Possible techniques for protecting vulnerable image, written or printed areas were also discussed. Most of the fixatives proposed for use are soluble in organic solvents. Many of the dyes, inks, etc. considered vulnerable to changes in pH will also be solvent sensitive, either during initial application or during removal of the fixative or protecting barrier material after treatment. Great interest therefore was shown in the technique used by McAusland, Petherbridge, Stevens and their colleagues — fixing with pure paraffin wax dissolved in petroleum ether.

There is a varied range of petroleum ethers (spirits) and the rate of evaporation of the solvent and hence penetration into the paper can be manipulated according to the boiling point of the ether selected — a major advantage. A range of paraffin waxes with different melting points is also available. Petherbridge discussed his developments of this technique in the temporary fixing of water-soluble Islamic manuscript inks in which the melting point of the paraffin wax selected enables the fixative to be removed after washing and associated treatments without the use of the solvent initially used to dissolve the wax. Instead, the artifact is placed in a bath of solvent in which the wax is not soluble and which has a boiling point higher than the wax's melting point. The bath is heated (all in conditions safe for the artifact and conservator) to a temperature slightly above the melting point of the wax fixative, which then floats

to the surface of the solvent bath from where it can be removed. The fixative can also be applied to written, painted or drawn areas so that it penetrates just enough of the surface of the support paper to fix (protect) the image area but leaving enough of the fibre substrate unpenetrated so that washing or other treatment water can penetrate the support (e.g. by capillary action). The paper can thus be washed (the process takes some time for passage of water to take place) with the image area protected and without the blotchiness after treatment which may occur as a consequence of a number of other fixing techniques due to differential washing and subsequent tone of fixed and unfixed areas with a relatively abrupt transition between them.

Thus there is a great range of properties of fixatives and solvents which can be juggled with, according to the needs and susceptibilities of the artifact being treated. One great advantage is that petroleum ethers are very poor solvents for most things except waxes. Therefore dyes, inks, natural pigments, etc. which might be shifted by solvents such as alcohols required for other fixative compounds could be protected using this fixative system, although it is essential to test first. As Petherbridge pointed out, however, research needs to be done on the possible effects of residual fixative on paper, pigments, inks, etc., and a possible problem of a cosmetic nature rather than a chemical/deteriorative one may be that even minor coatings of residual fixatives may cause the paper original to pick up (or reflect) dirt and soiling at a different rate from adjacent unfixed areas and so utimately cause the formation of slightly differently coloured or toned areas on ageing.

McAusland, Stevens, Petherbridge, Bayley and Segal all gave practical illustrations of the method's working advantages and publication of the method and further investigation was urged.

Although nothing very positive came out of the discussion concerning the prediction of likely colour changes, it was clear that very many conservators have chosen not to deacidify coloured material — especially art on paper. The consensus was that such changes are unacceptable.

A further aspect of possible alkali-related colour changes discussed was those occurring in the long term, especially in storage. Thomas queried whether long-term changes were likely following deacidification even if nothing happened immediately on treatment. Keyes cited the case of a Japanese print which had been reinforced all over with an alkaline Japanese paper. Subsequently a colour change occurred in alkali-vulnerable pigments. This led her to ask whether long-term storage with an artifact in contact with alkaline tissue and in alkaline mounting boards could lead to similar colour changes — especially in material which had intentionally *not* been deacidified for fear of colour change. This is an important area for systematic investigation. Items which have been mounted in alkaline board should be checked regularly, whether stored in the dark or placed on exhibition. Any changes then found could be communicated to colleagues.

Petherbridge noted cases of greater vulnerability to mould attack in alkaline boards than in old acid mounts, all kept under the same environmental conditions. He explained that the latter were those of the interior of traditional Greek-island buildings whose spaces were all painted with thick coats of whitewash, forming a calcium carbonate layer. Calcium carbonate dust is a feature of such rooms. In such environments there are certain characteristic fungal infestations which can flourish on alkaline surfaces (which brings to mind the characteristic pink/purple fungal infestations characteristic of parchment and vellum manuscripts in these areas — also on an alkaline substrate). These fungi seem to have found a more sympathetic environment in alkaline boards than in acid ones. Hey suggested that a contributory factor could be the greater moisture content in alkaline boards than in hard-sized acid mounts. If such a difference did exist it might be sufficient to promote mould growth. This could be checked using a moisture meter, using RH cards to monitor wall-surface conditions.

Aspects of washing without deacidification

Conference discussions made it clear that washing of papers without deacidification was a widespread practice, some warnings against which have already been given[1] but amplification is perhaps necessary.

If a paper has a high alkaline reserve then it is possible that after careful washing it will still be alkaline in nature. However, in the case of an acid paper washing may remove soluble acidity but it is unlikely to turn the paper into an alkaline one. Aluminium in the paper, bleaching and the presence of heavy metals which could have oxidized the cellulose-producing carboxyl groups are causes which will make paper acidic (washing will not remove all aluminium from paper). Left unneutralized, this acidity is self-generating[3] and, as Williams has recently pointed out[10], even a paper brought close to neutral pH by washing may rapidly degrade. This is a particular problem with art-on

paper which has been exhibited for a considerable length of time, since the effect of light on an acid paper is to promote accelerated deterioration. A more extensive study of the effects of washing only (without subsequent deacidification) was carried out by Tang and Jones[11] while has shown[12] that even a badly degraded paper will benefit from deacidification. In this context it might be useful to draw attention to some recent recommendations[13] that mending paper should have a pH of 5.5 upwards. *This is not good enough.* With time, acidity will increase in the more acid mending paper (see Williams for graphs on experimental rates[10]), be transferred to the mended paper and eventually offset onto adjacent leaves. We have all seen the consequences of acid mends in the past. It is not a practice that should be perpetuated in these more thinking days.

A frequent retort to criticism of the practice of washing only (without subsequent deacidification) is that, of course, if such is the practice then regular checking on condition is essential and that, consequently, any conditions requiring new treatment would be observed well in time because of these monitoring operations. However, discussions at the Cambridge 1980 Conference made it clear that, depending on storage conditions, many felt that monitoring inspections more often than at five-year intervals were not felt necessary . . . but is this practicable? — certainly not for a busy archives or library. Could a conservator working for a private clientele, including dealers, seriously consider the possibility of tracking down items every five years, checking pH values and then perhaps rewashing, re-mending, remounting, etc? It would seem a viable practice only for a small closed collection — even if one did disregard possible harm to the item through repeated handling. Anyone deciding to wash only without subsequent deacidification really must think through this side to the argument.

Characteristics of washing water

The use of de-ionized water for the washing of paper is becoming more widespread, but it is not always well understood why it should be necessary, and this was an aspect of conference discussion. Quite simply, it is in order to prevent the deposition of iron and especially copper in paper. Both metals are very common impurities in water and both degrade cellulose. Therefore it is essential not to increase their concentration in paper during restoration and conservation. Before deciding to de-ionize water in the conservation workshop, an analysis of the local water supply should be obtained in order to determine the actual iron/copper content (and also that of chlorine which could be present in recycled water).

If water is de-ionized it will have a low pH — even as low as pH 4. If water of low pH is used for washing, then not only will washing be less effective (because paper acidity will be removed less easily) but beneficial alkaline carbonates could be removed from the paper at the same time. This is not a contradictory set of effects — it is possible, and extremely common with earlier papers, to have acid areas and alkaline areas in the same leaf. Therefore it is strongly advised that, before washing paper, de-ionized water should be brought back at least to the neutral pH point. Tang[14] describes one complicated way of doing this. Another way would be to add solid calcium carbonate (marble chips) — a method originating with the Smithsonian Institution and used by Vitale. Even simpler is the technique of adding calcium hydroxide solution (Hofer; Hey[1]). In all cases it should be borne in mind that if a given quantity of water is being used to wash a batch of papers, then the pH will drop rapidly as the alkalinity is consumed by the papers' acidity. Frequent changes of water will be necessary. This low concentration of alkali has not been found to give rise to any of the handling problems which are sometimes found with normal-strength deacidification solutions (and which caused so much conference discussion) — and greatly feared.

The presence of heavy metals in paper (especially iron and copper)

It is becoming fashionable to analyse papers for their metal content before deciding what to do in way of conservation. This is not a very practicable procedure, as it is expensive, time-consuming and frequently destructive. Every leaf cannot be analysed all over in routine conservation practice. It is far better to appreciate that all papers contain iron to a greater or lesser extent (because of the nature of cellulose, the technology of preparation — especially where alum is used, where iron is a very common impurity). Many handmade papers will contain copper from the sizing utensils used. Nineteenth and twentieth-century papers will contain metals, either from the original wood used as the fibre source or dissolved out during manufacture (acid stock). If the metals are in an active state, they will have made their presence apparent by local or all-over discolouration of the paper of which they are a constituent.

Both iron and copper degrade cellulose more rapidly in the presence of moisture. Washing alone could reactivate iron which had been in a aquiescent state. McAusland said that she found this as a phenomenon in modern papers but not with older handmade ones. This could be due to residual alkalinity in the latter. The more slowly papers dry, the more likely is it that reactivation of iron will occur. Therefore, both when washing only and after deacidification, papers should be dried as rapidly as the characteristics of the item permit (but not with heat). It should also go without saying that while wet paper should never be in contact with metals, good drying practice alone will not safeguard paper during future storage contact.

The importance of alkaline conditions in slowing down iron-catalysed cellulose degradation has been shown by Hey[15] and by Williams[10]. Williams also demonstrated that alkalis will not stop copper-catalysed degradation — a point made by Hey[16] with respect to copper pigment-induced degradation and by Indian conservators, after observing the effects of treatment in practice.[17] This is a problem which needs tackling in another way. The writer is exceedingly grateful that earlier, unsubstantiated claims concerning magnesium's alleged ability to nullify copper's degradative effects have now been quietly dropped.

Early papers contained iron as a natural impurity. During the nineteenth and twentieth centuries it was customary practice to add iron pigments to certain drawing papers to tint them. McAusland explained that such papers used by Braque and Picasso, amongst others, developed localized mould with associated staining. Stevens explained how bleaching could remove the stains giving very acceptable visual results. It was noted however, that in the long term these areas may turn whiter than their surroundings — attributed by Segal to non-removal of the bleaching agent employed. Today conservators are having to deal with such problems of earlier bleaching operations. It would be useful in cases where this phenomenon occurs to learn if pH differences are found between the differently toned areas.

Washing and deacidifying practices

Conferences are an admirable forum for exchanging information on working practices — and problems. Float washing is very popular for art-on-paper when liquid water on the upper surface of the paper (the image area) is to be avoided. Its effectiveness in the actual washing of paper is queried. As with all paper washing, efficiency is related to water penetration of the paper. Alcohol mixtures[1] can be very helpful in promoting penetration, provided all image components can withstand the solvent. Subsequent deacidification using the float technique will be much more effective if the paper is first washed well, then put immediately into the deacidification solution. Effectiveness can be checked by first treating scraps of similar papers, drying them, then using indicator solutions on both sides. This will give an idea of the final pH differential through the paper. When vulnerability to alkaline solutions is possible, efficient pre-washing (if the item permits it) will reduce the need for long periods of immersion in alkaline solution. Pick-up of the alkaline compound is rapid.

Problems with surface deposits of deacidifying agents

Deposits on the paper and image (painted, drawn, written or printed) surface after deacidification treatment are particularly undesirable with art-on-paper when they can be visually as well as tactilely offensive. During the discussion session concerned a variety of cases were advanced for the formation and character of such deposits. Only one conservator had observed this phenomenon to occur whatever deacidification agent was used. Others observed that in their experience it was more likely to occur with solutions containing high concentrations of magnesium bicarbonate. Futernick observed that if a crystalline deposit is found, in many cases it can be removed by soaking the paper in carbon dioxide water (carbon dioxide bubbled through distilled water) with a lid on the container while soaking until the deposit disappears. McAusland noted that in some cases only the extreme measure of applying a very dilute acid solution would remove the defacing deposit.

Apart from suggestions for removal of the deposits, various suggestions were made for preventing their appearance. One was to dry the paper face downwards. Any crystals might then form on the verso side (opposite the image side). Another suggestion was to dry the paper between blotting paper. In this method excess deacidification solution moves into the blotting paper and crystals form there, not on the item being deacidified. Another was to pass the paper through clear water after deacidification, or to use a very weak (*c* 0.5%) magnesium bicarbonate solution. These may all work but, as was pointed out by Petherbridge, they may lower the final alkaline reserve levels in the paper and how long these will function as a buffer?

The Library of Congress Preservation Office originally suggested 3% as the minimum alkaline deposit after treatment[18]. Now a level of 1% has been suggested as representing 400 years' protection[10]. The writer would prefer to be more flexible and considers that, if a paper is not severely discoloured, good deacidification processing, especially thorough wetting, and good storage conditions should provide adequate protection. If iron-induced degradation or iron-based inks are present then a higher percentage of deposit, perhaps from double deacidification treatment, would be preferable.[15] When a low level of deposit is deliberately chosen then regular checking of the item's condition is essential (as is recommended when items have been washed only — without subsequent deacidification).

Segal queried the nature of a crystalline deposit she had observed over an acid ink area (but not on the paper itself). Hey suggested that it could be a local high deposit of magnesium sulphate. Brannahl has published photographs of this[19]. It would be useful to have an analysis carried out of this feature if anyone observing it has access to non-destructive analytical facilities. If this suggestion regarding the chemical composition of such a deposit is correct, then thorough washing of the paper to remove excess sulphuric acid before deacidification would reduce the likelihood of its appearance.

Spray deacidification

Deacidification by spraying as a technique led to much discussion. After so much emphasis had been placed on the need for good penetration of the deacidifying solution (see above) it was queried whether spraying could indeed do any good. It could perhaps be better than nothing but problems may well arise. For example, an aqueous solution of magnesium bicarbonate could lose its carbon dioxide while passing through the air as a spray. It would then deposit on the surface of the paper as a suspension of basic magnesium carbonate. Little or no penetration into the paper would occur and little or no deacidification of the paper would result. Use of an airless spray gun would improve matters. Prior dampening of the paper would increase penetration of the deacidification solution. It must be remembered, however, that all papers contain soluble impurities. These are shifted by water — but spraying is usually carried out on unwashed papers. If such paper is dampened to encourage penetration and spraying for deacidification is then thorough (to encourage as complete deacidification of the paper substrate as possible), then the amount of water present may well be enough to shift soluble impurities, so causing unpleasant streaking on drying.

Non-aqueous spraying, if not carried out carefully, can also lead to problems, as Riley explained in relation to heavy surface deposits occurring when using Wei T'o No. 3 spray solution in the wrong way. Non-aqueous spray solutions evaporate fairly rapidly, especially when propelled through the air. There is therefore more likelihood of the deacidificant being deposited on the surface of the paper being sprayed. The precipitation problem observed by Riley has the potential to be more pronounced with the Wei T'o sprays because the concentration of deacidifying agents is much higher than would be the case with barium hydroxide, the other non-aqueous possibility in this context — although even this does cause some problems according to Harding. In addition, some cellulose degradation products are organic solvent-soluble and heavy spraying could also lead to streaking on drying. According to Waters, the Library of Congress has now abandoned spray deacidification and Hey prefers that the technique be discontinued as a first deacidification treatment. Spraying, however, can be useful as a way of 'topping up' alkaline reserve in materials which have already been washed/deacidified or deacidified by immersion in a non-aqueous deacidifying solution. This is particularly helpful for iron-containing paper.[15]

Waters referred to poor penetration when methylmagnesium carbonate solutions are brushed onto paper, even when it would appear that the solution had penetrated right through the paper — a pH of 8 on the brushed side and 5 on the reverse was not uncommon. Brushing had been suggested as a way[20] of treating the back of art-on-paper when concern for the image makes immersion deacidification unacceptable. Failure of solutions to penetrate through brushing was described by Kelly and Fowler[21] and demonstrated by Hey during the discussion concerning samples which had been subjected to accelerated ageing. Waters mentioned that increasing the proportion of alcohol in the methylmagnesium carbonate solution would improve its penetration. However, as one of the advantages of these solutions is that they can be used over many soluble modern inks which 'bleed' in other solvents, this advantage could well be lost if the alcohol content is increased.

Treatment of samples with methylmagnesium carbonate solutions has produced excellent results when total penetration to all surfaces has occurred. Immersion application is therefore strongly

advised. Brushing or spraying could then be used as a means for increasing alkaline reserve only.[15]

The discussion sessions on the subject of deacidification were extremely valuable because conservators were willing to discuss freely their working experiences and to exchange information on successes and failures. However, as stated at the beginning of this account, a general impression in retrospect is that, while there are a number of important new areas for investigation being revealed, much of the information required by conservators to solve problems in this subject is, in fact, available but is not always as widely disseminated as could be desired.

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PART VII

NOTES ON THE CONTRIBUTORS

Esther Boyd Alkalay was born in 1925 in Sofia, Bulgaria. She graduated in Chemistry at the University of Sofia in 1953. In 1956 she established the Laboratory of Restoration and Conservation in the National Library in Sofia and remained as head until 1969, when she emigrated to Israel.

In Israel she established a similar laboratory in the Jewish National and University Library in Jerusalem. She constructed four leaf-casting machines in Bulgaria and six in Israel.

Since 1978 she has lived in London; she pays frequent visits to Jerusalem to act as a consultant in her laboratory.

Helmut Bansa. 1965. PhD in history. 1968-1971, additional studies in chemistry. 1972, academic degree in librarianship. Since 1972 Head of the Institut für Buch-und Handschnenrestaurierang an der Bayerischen Staats-bibliothek, Munich. Lecturer in book techniques at the Munich Library Schools.

James R. Briggs. Born in Croydon 1930. BSc (Eng). E.Eng. MI Mech E, FCIBS, MIEE, M Cons E. Educated at Ashford Grammar School in Kent, the Royal Navy Engineering Artificer Training Establishment at Plymouth and Arbroath and at the Northampton College of Advanced Technology of London University, now City University, London, gaining a BSc (Eng) 1st Class Honours in 1958. Trained with G. H. Buckle & Partners. Consulting Engineers of London between 1948 to 1962 as student and senior engineer. In 1962 became a Partner with A. K. McAusian & Partners of Belfast and Liverpool until, in 1968, the practice James R. Briggs & Associates was formed of which he is the Senior Partner.

Helen Diana Burgess. Born in Lethbridge, Alberta, Canada. Batchelor's degree in chemistry, University of Lethbridge, Lethbridge, Alberta, specializing in organic chemistry. Master of Science degree in chemistry from the University of British Columbia, Vancouver, specializing in protein chemistry. Master of Art Conservation degree with the Art Conservation Programme, Queen's University, Kingston, Ontario, specializing in conservation science. Thesis was concerned with the degradation of cellulose during conservation bleaching treatments. At present working with the Conservation Processes Research section of the Canadian Conservation Institute, Ottawa, where involved in studies concerning the conservation of paper artifacts. These studies deal with the effects upon the paper artifacts of specific conservation treatments presently being used by the conservator, as well as the development of new conservation methods and procedures.

Anthony G. Cains. 1953-1960; served an apprenticeship to the London trade bindery of Messrs. E. A. Neale. Studied at the London School of Printing and Graphic Arts and at the Central School of Art and Crafts and also at Guildford School of Art under the late William Matthews, on whose recommendation he became an assistant to Sydney M. Cockerell of Douglas Cockerell & Son (1961-1964). This was followed by a short period at the HMSO British Museum Bindery and part-time teaching at Camberwell School of Art and Crafts under the late John Corderoy, the London College of Printing and Farnham School of Art. At the suggestion of John Corderoy, he volunteered in 1966 for flood rescue work in Florence, subsequently supported by the British Art and Archive Rescue Fund, and became Technical Director to the Biblioteca Nazionale Centrale of Florence, a post funded by the American Committee to Rescue Italian Art (CRIA). In 1972 he was invited to design, establish and head a laboratory at Trinity College Library, Dublin.

Julian Clare. Joined the India Office Library conservation section in August 1967 for training with Fred Marsh in the field of paper conservation. Promoted in 1972 and is now specializing in the conservation of illuminated books and manuscripts.

David Cooper. Studied chemistry at Cambridge and the University of East Anglia. Post-doctoral research in chemistry followed at the Dyson Perrin Laboratory in Oxford. Since 1972 he has been the assistant librarian at Corpus Christi College in Oxford, and is now (1980) consultant at the Conservation Section of the Bodleian Library, Oxford.

Christopher Clarkson. After gaining his Diploma in Graphic Design specializing in 'Writing and Illumination' and 'Letter Cutting' at Camberwell School of Art and Crafts, he freelanced for two years. He then entered The Royal College of Art gaining an ARCFA 'Fine Bookbinding' and a travelling scholarship which he spent drawing in Greece. Clarkson has taught book design and book production, engraving and calligraphy in several art departments including Camberwell and Farnham Colleges of Art. He has worked for Sydney Cockerell and was amongst the first volunteers in the Florence flood rescue operation (1966). In 1972 he was appointed Head of Rare Book Preservation at the Library of Congress, Washington, DC, moving to the noted collection of the Walters Art Gallery in 1977. Clarkson has been the Conservation Officer at the Bodleian Library, Oxford, since September 1979. He has been a conservation consultant to many collections with manuscripts and rare books.

Vincent **Daniels**, BSc., PhD., MRIC, C Chem. Born 1948. Obtained his BSc at University College, Cardiff, and proceeded to perform research work on the degradation of polymers and their subsequent reactions in solution. After a period of post-doctoral research into electron transfer reactions he joined the British Museum Research Laboratory in 1974 to work on aspects of paper conservation. In 1976 he moved to the newly created Department of Conservation where he is Principal Scientific Officer in a multidisciplinary team studying conservation of all the materials of antiquity.

Peter G. Ellement. Obtained his BSc (Leather Science) from Leeds University in 1960. He gained teaching experience in the Leather Department, Northampton College of Technology and was appointed Head of the Science Department, National Leathersellers College, London in 1966. When the Leathersellers College moved to Northampton in 1977 to merge with the Leather Department, Nene College — to form the National Leathersellers Centre — Peter Ellement was appointed Head of Leather Studies. He is a Principal Lecturer and is responsible for teaching Leather Science.

Hon. Secretary of the Society of Leather Technologists and Chemists for 10 years, a member of the Footwear, Leather and Fur Skin Industry Training Board and a member of the Council of the British Leather Manufacturers Research Association and the Leather Conservation Centre.

Wilfried Feindt. Born November 1943 in Mettingen, Westphalia, West Germany. Attended school in Mittingen and Osnabrück. Studied chemistry and geography at the Technical University of Brunswick. Professional archivist training at Osnabrück and Hanover. Archivist at the State Archives in Bückeburg, Lower Saxony, since 1974. Responsible for the training of restorers, for the application of all technical developments in the restoration workshop for mass restoration at Bückeburg, and for the research programmes in the field of restoration. Corresponding member of the International Council on Archives Conservation and Restoration Committee.

David F. Foxon. Born in 1923, educated at Kingswood School, Bath and Magdalen College, Oxford. Assistant Keeper, British Museum Library 1950-1965; Professor, Department of English, Queen's University, Kingston, Ontario 1965-1968; Reader in Textual Criticism and Fellow of Wadham College, Oxford since 1968. Fellow of the British Academy; President of the Bibliographical Society. Author of *English Verse, 1701-1750: a catalogue*, Cambridge, 1975.

David Grattan, BSc in Chemistry, Imperial College of Science and Technology, University of London, 1968. 1968-1970: Research Chemist, International Synthetic Rubber Co., Hampshire. 1970-1973; PhD in polymer chemistry, University of Keele. 1973-1977; Research Fellowship in Photochemistry, then a Research Associateship in polymer photodegradation at the National Research Council of Canada, Ottawa. 1977; Senior Conservation Scientist, Canadian Conservation Institute, National Museums Canada, Ottawa.

Betty M. Haines. Received a Bachelor of Science Degree in botany, zoology and chemistry from the University of London in 1949. The same year she joined the Biology Department of the British Leather Manufacturer's Research Association and in 1968 became Head of this department where both light and scanning electron microscopy are used in the investigation of charges in both skin and leather brought about during leather manufacture and during the subsequent use of the leather.

Eric Harding. Joined the photographic department of the Victoria and Albert Museum, London in 1946. In 1950, on his return from National Service in the RAF, he began his apprenticeship in prints and drawings conservation, remaining at the V & A until 1965. In 1966 he took charge of prints and drawings and watercolours conservation at the British Museum as Senior Conservator, and was responsible for re-designing and re-equipping the new conservation studio, which was completed in October 1967. In 1972 Eric Harding was appointed to the newly created grade of Chief Conservation Officer. In 1975, on centralization of conservation services at the British

Museum and the forming of the Department of Conservation and Technical Services, he also became responsible for the Oriental paintings and print conservation section. Fellow of the International Institute for Conservation of Historic and Artistic Works.

Margaret Hey. After studying chemistry at Oxford University, Margaret Hey joined the Scientific Department, National Gallery, London, where she was particularly concerned with the application of synthetic materials during restoration. Since entering the field of library and archival conservation she worked at Imperial College of Science and Technology (Dept. of Mechanical Engineering) with the short lived Library Materials Conservation Group (funded by the Council of Library Resources Inc., USA) then in the Biblioteca Nazionale Centrale, Florence. Three years' chemical research at the Istituto di Patologia del Libro, Rome (also funded by CLR Inc.) followed. A short period in the Conservation Department, Trinity College Library, Dublin preceded 18 months as Visiting Chemist in the Preservation Office, Library of Congress, Washington, DC.

Judith H. Hofenk de Graaf. Born 1936. MO chemistry (Gemeente Universiteit), B.A. history (Vrije Universiteit). Worked at the TNO fibre institute, specializing in textile chemistry, 1955-60; conservation research and analysis of dyestuffs at the Technical University, Delft, under Dr. J. E. Leene, 1960-63; in 1963 joined the Central Research Laboratory for Objects of Art and Science, Amsterdam, where she is Head of the Department of Natural Polymers. Fellow of the International Institute for Conservation of Historic and Artistic Works.

Dr Hans-H. Hofer. 1970, PhD in chemistry. 1970-1974, head of research and development in a German papermill for coated papers. 1975-1979, Lecturer in Paper Converting and since 1979 Professor in Paper Converting, Paper Chemistry and Paper Coating at the Fachhochscule München.

Craig Jensen. A native of southern California, did his undergraduate work in Asian Studies and Industrial and Graphic Arts at Brigham Young University. While doing his college studies he did independent research into the methods and techniques of hand papermaking and conservation related studies. Jensen interned at the Restoration Office of the Library of Congress and studied under Tom Albro, Don Etherington and Peter Waters. He also attended workshops given by Theo and Anne Kahle in binding and conservation at their Capricornus School in Berkeley, California. Jensen joined the Brigham Young University library staff in January 1977. He is now Conservator at the Humanities Research Center, University of Texas at Austin.

George B. Kelly, Jr. Born in Washington, DC. Graduated from the University of Maryland in 1937. Worked for many years at the Library of Congress as a research chemist in the laboratory of the Preservation Office. Previously employed by Union Carbide Corp. at their research centre in South Charleston, West Virginia. Chemical background covers a number of diverse fields including mineral recovery, improving the efficiency of oil filters, development of rocket fuels for the space programme, water soluble polymers and new chemicals for the paper industry. Since 1972 he has been working on the development of non-aqueous deacidification of paper and vapour phase deacidification processes in particular. He has been granted eight patents and has numerous publications in the field of paper and paper conservation.

Yash Pal Kathpalia. Conservation specialist. Honorary Life Member, Association of Archivists, Caracas, Venezuela; Member of the International Council of Archives; Member of the Society of Archivists (UK); Member of the American Society of Archivists; Honorary Member of the Association for the Study of Conservation of Cultural Property in India; Chairman of the International Council on Archives Conservation and Restoration Committee; Lecturer in Restoration, Diploma Course in Conservation and Archival Science. Institute of Archival Training, New Delhi, India.

Keiko Mizushima Keyes. Born and raised in Japan. K. M. Keyes presently lives in California engaged in conservation of works of art on paper as an independent conservator. She completed her basic training in 1967 under apprenticeship with Mr Iwataro Oka, President of Mounters' Association for National Treasures and Important Cultural Properties, in Kyota, Japan. In subsequent international travel while working for R. E. Lewis, Inc., she visited professional colleagues in museum laboratories and private work studios in the USA, Europe and Japan and exchanged opinions about current problems in paper conservation. She taught paper conservation at the Cooperstown Graduate Program for the school year 1976-1977, worked as conservation specialist at the Achenbach Foundation Conservation Laboratory in California Palace of the Legion of Honor, and acted as consultant to various institutions and private collections including Musëes Rovaux et d'Histoire in Brussels, Belgium; Intermuseum Laboratory in Oberlin, Ohio; Cleveland Museum of Art and Williamstown Regional Art Conservation Laboratory.

Carolyn King. Read biochemistry at Oxford. PhD from University College Medical School. Worked as post-doctoral research assistant for Dr W. E. van Heyningen, 1970-1979.

Dr Adel Koura. Born 26 October 1943 in Egypt. Holds a BSc degree (1964) and MSc (1969) from the University of

Ains-Shams-Cairo and Dr. rer. nat. (1972) from the Technical University of Magdeburg, GDR.

Joined the National Research Centre, Cairo, Cellulose and Paper Department from 1965-1968. From 1968 to 1972 in the Polymer-Chemistry Institute of Teltow-Seehof, GDR. In 1972 joined the Cellulose and Paper Department of the National Research Centre, Cairo, and in 1976 came to the Technical University Darmstadt, GFR, Institute of Macromolecular Chemistry, Cellulose and Paper Department. Has published about 30 papers and patents in the wood, cellulose and paper chemistry area, nine publications on ageing of paper.

Dr Thomas Krause. Professor. Dr. rer. nat. Born 24 April 1926 in Memel, Lithuania. After school and war participation, study of textile and cellulose chemistry and work in the pulp and paper industry. Dr. rer. nat. in 1964 with a thesis on pulp manufacture from poplar wood at Technical University, Darmstadt. Since 1972 professor at the Institute of Macromolecular Chemistry, in charge of the Cellulose and Paper Chemistry Department, Ca. 50 publications in this field.

John Maggs. Born 1926, Radlett, Herts. Eldest son of Frank Maggs, bookseller; grandson of Ben Maggs, bookseller and great grandson of Uriah Maggs, bookseller, who came to London from Somerset in about 1860. Educated at Edge Grove Preparatory School, Radlett and at Aldenham, Elstree. War service 1944-1947 in Fleet Air Arm as Leading Airman. Treasurer of the Hackluyt Society, Council Member of the Royal Geographical Society and Honorary Librarian of the Cruising Society.

J. Clifford McCawley. BSc, MSc, FSA Scot. Formerly Chief of Analytical Research, Parks Canada, presently Acting Chief, Regional Services, CCI (was Chief of Conservation Processes Research until 1979). Research interests: waterlogged wood, paper, metallic corrosion and inorganic analysis.

Frederick Marsh. Joined the Public Record Office in January 1957 as a trainee craftsman. Moved to the India Office Library in May 1962 to start a conservation section. Promoted in 1969 with the responsibility of designing and equipping a new conservation department for the combined India Office Library and Records. Promoted to Senior Conservation Officer in 1975 and now specializing in the conservation of illuminated manuscripts and Indian and Persian miniatures. Fellow of the International Institute for Conservation of Historic and Artistic Works.

Dag-Ernst Petersen. Born 1942 at Cologne, West Germany. 1963-1966: bookbinding apprenticeship. 1965: volunteer, Institute for Restoration, Bavarian State Library, Munich, working with Butz, Jackel and Ziegler. 1966-1968: bookbinder at the Legatoria Artistica, Ascona, Switzerland. 1966: volunteer, Institute of Restoration, National Library, Vienna, under Professor Otto Wachter. 1968-1969: student at the Ecole Estienne, Paris under Professor R. Mondange and restorer at a private bindery. 1969-1970: studied as master bookbinder at the Meisterschule für Buchbinder, Munich. 1971-1973: studied at the Fachschule für Cheme (Chemotechniker). Since 1973, conservator and restorer of books and works of art on paper, Duke August Library, Wolfenbüttel.

Guy Petherbridge. Born 1944, Brisbane, Australia. Educated at University of Queensland; National Art School, Sydney; University of Florence and Camberwell School of Art and Crafts, London (paper conservation). Specializes in the conservation and technical history of Christian, Oriental and Islamic manuscripts. Consultant to many institutions with holdings of such material. 1978: Technical Cooperation Officer, British Ministry of Overseas Development, Falkland Islands, South Atlantic. 1978-1981: Consultant Curator/Conservator of Islamic bookbindings, Oriental Institute Museum, University of Chicago, under NEH grant. 1979-: Grantee (Biddle Foundation and Council of Library Resources) with Dr John Sharpe, Duke University Library to research and publish a history of traditional Greek bookbindings based on the collection of the Monastery of Saint John, Patmos. 1983-1984: Scientific Advisor, Directorate of Scientific Policy, Greek Ministry of Research and Development. After collaborating with Denis Blunn and the Spanish National Centre for the Restoration of Books and documents in developing non-adhesive leaf-casting methods, was 1979-1981 consultant to the Canadian Conservation Institute, Otawa, directing the establishment of a leaf-casting unit and training personnel. A founding editor of *The Conservator*, Journal of the United Kingdom Institute for Conservation; Founding Editor of *The Paper Conservator* and *Paper Conservation News* and Executive Committee member, Institute of Paper Conservation 1976-1983. Fellow of the Royal Asiatic Society.

Peter Menno Poldervaart.Born in Schagen in 1943. Trained at the Prentenkaninet, Rijksmuseum, Amsterdam, 1965-1966, and at the Institut Neerlandais (Fondation Custodia, Paris. 1966-1968: Undertook a course into the theoretical background to the restoration and conservation of paper at the Centraal Loboratorium, Amsterdam. 1970-1971: in private paper conservation practice working for museums, art galleries, etc. Headed the Nova Zembla project.

Johanne St Hilaire. 1976: received a DEC in Biochemical Techniques and joined ERI Pharmaceuticals Montreal, later transferring to the Clinical Research Institute where she worked on the synthesis, purification and determination of activity of peptides. Came to CCI in 1979 and worked on the Enzyme Project.

Judith Segal. Studied bookbinding with Charles McNally at Dartington and with Lucie Weil in Paris. She has been Senior Conservator at Bodleian Library, Oxford, since 1969. She is a Member of the Executive Committee of the Institute of Paper Conservation.

Richard Daniel Smith. Born South Bethlehem, Pennsylvania, 1927. BS Pennsylvania State University, 1952: MA University of Denver. 1964: PhD University of Chicago, 1970: Registered Professional Engineer, State of Ohio, 1971: President, Wei T'o Associates, Inc., Matteson, Illinois. Instructor, Graduate Library School, University of Chicago. Consultant, Public Archives of Canada. Associate Editor *Restaurator.* Member: American Association for State and Local History, American Chemical Society, American Library Association, Guild of Book Workers, Institute of Paper Conservation, Society of American Archivists, Special Libraries Association. Fellow: American Institute for Conservation of Historic and Artistic Works.

Phillip Stevens. 1963: joined Messrs Craddock & Barnard, old master print dealers in London as an apprentice conservator and restorer. 1967: became an independent restorer and conservator in London. For many years lecturer in prints and drawings conservation at Camberwell School of Art and Crafts, London. Specializes in the conservation of Indian miniatures.

Alice Swan. Conservator of photographs. Master's degree in photography from California State University at San Fransisco. Studied paper conservation with Inge Lise Eckmann and photographic chemistry with Dr R. Francis at Rochester Institute of Technology. Held a photographic conservation internship at the International Museum of Photography at George Eastman House, later becoming their Conservator. She has researched early photographic processes, particularly salt prints and daguerrotypes, having made a study of the latter while a guest researcher at the National Bureau of Standards.

S. John Teague. BSc. (Econ). Librarian, City University, London, since 1973. Formerly Librarian, Chelsea College, London. Earlier career in public libraries. Fellow of the Library Association, Chairman, Microfilm Association of Great Britain, 1959-1980: Honorary Editor of *Microdot,* 1974-1979: on Editorial Board of *Microform Review.* Publications include: *Microform Librarianship,* 2nd edn, 1979; *The City University: a History,* 1980; *History of Chelsea College* (co-author). General interests: nineteenth century history.

David H. Tuck obtained a Diploma in Leather technology and his Associateship of the Leathersellers College, London, in 1937. He obtained his practical tanning experience at the Midland Leather Company, Rochdale and at J. Hewitt, Edinburgh. In 1974 he joined the teaching staff at the Leathersellers College, London and moved with the College when it merged with the Leather Department of Nene College to form the National Leathersellers Centre, Nene College. David Tuck is a Senior Lecturer and is responsible for teaching Leather Technology in the Leather Centre.

His other interests are in Rural Tanning and Retail Staff Training.

Vicente Viñas. Chief, Technical Department, National Centre for the Restoration of Books and Documents, Madrid, a position he has held since the Centre's inception in 1969. Currently he teaches at the Centre's School for Restoration Technicans and the State-run School of Arts and Crafts. He is a member of the Executive Committee of ICOM, national branch, and has been a consultant for UNESCO and the Organization of American States on the subjects related to the installation of restoration laboratories in the Caribbean. In addition to these activities he is the author of several articles on paper conservation published in the Spanish-language periodicals.

Willem P. van Oort. Born 1919. 1935-1946: worked in a newspaper printing office. 1946-1964: paper restorer at the Print Room of the Rijksmuseum, Amsterdam. 1964-1970: independent paper restoration practice. 1970-: Chief Restorer in paper conservation, Print Room, Rijksmuseum.

Peter Zegers. Born Amsterdam, the Netherlands. Graduated from Amsterdamse Grafiese School. 1962-1963 internship with W. F. van Ort and P. Busink at the Rijks-sprentenkabinet, Rijksmuseum, Amsterdam. 1962-1967, Maritiem Museum, 'Prins Hendrik', Rotterdam. 1967-1970: Royal Ontario Museum, University of Toronto, Ontario, Canada. 1970-1974: Yale Centre for British Art and British Studies, Yale University, New Haven, Connecticut, USA. 1974-: National Gallery of Canada, Restoration and Conservation Laboratory, Ottawa, Ontario, Canada.

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