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# Some Special Cases of Biological Deterioration of Books

*by* YU. P. NYUKSHA

Fungi are exceptionally abundant on the Earth. They have a variety of fermentive complexes and high ecological adaptability which gives them the leading place in damaging library and archives materials. Our knowledge of the biology of fungi which attack materials allows a conclusion about the role of separate representatives in their growth in book stacks. We have shown this, using as the example *Aspergillus flavus* Lk., whose participation in the destruction of various book materials has been confirmed by many facts, observations and investigations.

According to Raper and Fennell,[1] the Aspergillus flavus group of the genus Aspergillus includes the following 9 species: *A. flavus* Lk., *A. parasiticus* Speare, *A. oryzae* (Ahlb.) Cohn, *A. zonatus* Kwon et Fennell, *A. clavato-flavus* Raper et Fennell, *A. tamarii* Kita, *A. flavo-furcatus* Batista et Maia, *A. subolivaceus* Raper et Fennell, and *A. avenaceus* G. Sm.

The fungi of the *A. flavus* group have been known as the inhabitants of soils in arid climatic zones. Indoors, their spores on paper germinate at a relative air humidity of 60–80% when the moisture content of the substrate hardly reaches 8%. *A flavus* is characterized by good viability in latent state and under conditions of increased temperature and osmotic pressure. The viability of the conidia of this fungus on paper indoors has been known to last for 12 years. The fungus did not die in salt solutions of high concentration and grew at a temperature of 45–48°C.

*A. flavus* is characterized by a comparatively rapid growth and spreading on the material. This feature of the species determines its abundance and high rate of book destruction. An investigation of book stacks, paper-making works and stores has indicated the highest percentage of attack by this species of fungi. In basements during WW II *A. flavus* was observed to have attacked the entire book stacks including not only books, but also metal shelves. Especially serious damage to materials caused by *A. flavus* and *A. oryzae* has been noted in books, files and boxes made using glue from wheat flour or hide glue. In the case of poor drying of materials *A. flavus* covered all surfaces entirely despite the fact that the relative air humidity in the room was not higher than 45%.

These fungi are distinguished by a high biological activity. *A. flavus* forms amylases, proteases, esterases, pectinases, certain cellulases and other ferments. More than 20 metabolites of these fungi have been studied and chemi-



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cally identified.[2] Among them are many acids and their derivatives, several nitrogen-containing cyclic compounds including amino compounds, uric and aspergillic acids and their derivatives, flavocol, acid-containing flavotoxins, penicillins, and many others. This biochemical activity is an adverse property enhancing the effect of damage to books and archives in the case of long-term storage.

Protease activity of *A. flavus* representatives isolated from paper has been studied. It proved to be almost independent of the pH level and is exhibited on many protein materials. For example, gelatine is liquefied by the fungus at a high rate: the process develops almost in a straight line at an angle of 60–70° to the abscissa axis carrying the time dimension. Hydrolysis of potato starch is performed by *A. flavus* with production of 1g of maltose per 10g of starch. A culture medium of the fungus reduces by 50% the viscosity of a 0.5% solution of natrium carboxymethyl cellulose. These properties enhance the viability of *A. flavus* in communities with other fungi having endoglucosidases responsible for the primary breaking down of cellulose. Because of the biological activity during co-habitation *A. flavus* affects the growth of other fungi.[3] For example, it strongly stimulates pigmentation in Myxotrichum deflexum on paper and suppresses the growth of Verticillium tenerum, Stachybotrys chartarum and other fungi.

*A. flavus* uses inaccessible sources of carbon including synthetic and natural complex ethers and carbon chain polymers (polyvinyl acetate, polyvinyl chloride, polyvinyl alcohol, polyethylene and other polyolefines).[4,5] The fungus grows on dispersions of polyvinyl acetate, polymethylmethacrylate, polyethylene, on film coatings of cellulose acetate and of methylcellulose and carboxymethyl cellulose. Paper laminated with polyethylene at a temperature of 110°C is attacked by *A. flavus*. The fungus spreads rapidly over the surface of the binding made from leather, cloth and polyvinyl chloride. It is very dangerous for products containing natural beeswax and paraffin.[6,7]

Paraffined paper which is widely used in many technological processes during restoration of books is readily affected by *A. flavus*, loses its water-repellant property and becomes yellowish. Commercial paraffined calico tape is rapidly destroyed because of fungal growth. The fungus is widely known to have affected technical cotton and other materials.

Characters and embossed work on waxen boards and seals disappear under the action of *A. flavus* which converts them into whitish powder resembling dry bread crumbs. Medieval seals were made from beeswax with the addition of resinous powder. They were protected against damage by the colouring substance called verdigris (main copper acetate) and cinnabar (mercuric sulphide). With time, these conserving agents deteriorated and the boards and




Fig. 1. Scanning electron micrographs of beeswax surface. 1a: × 720, 1b: × 2000.

Fig. 1. Microphotographies prises au microscope électronique à balayage de la surface de cire d'abeille.

Abb. 1. Abtasten einer Bienenwachsfläche mittels elektronischer Mikrobilder.

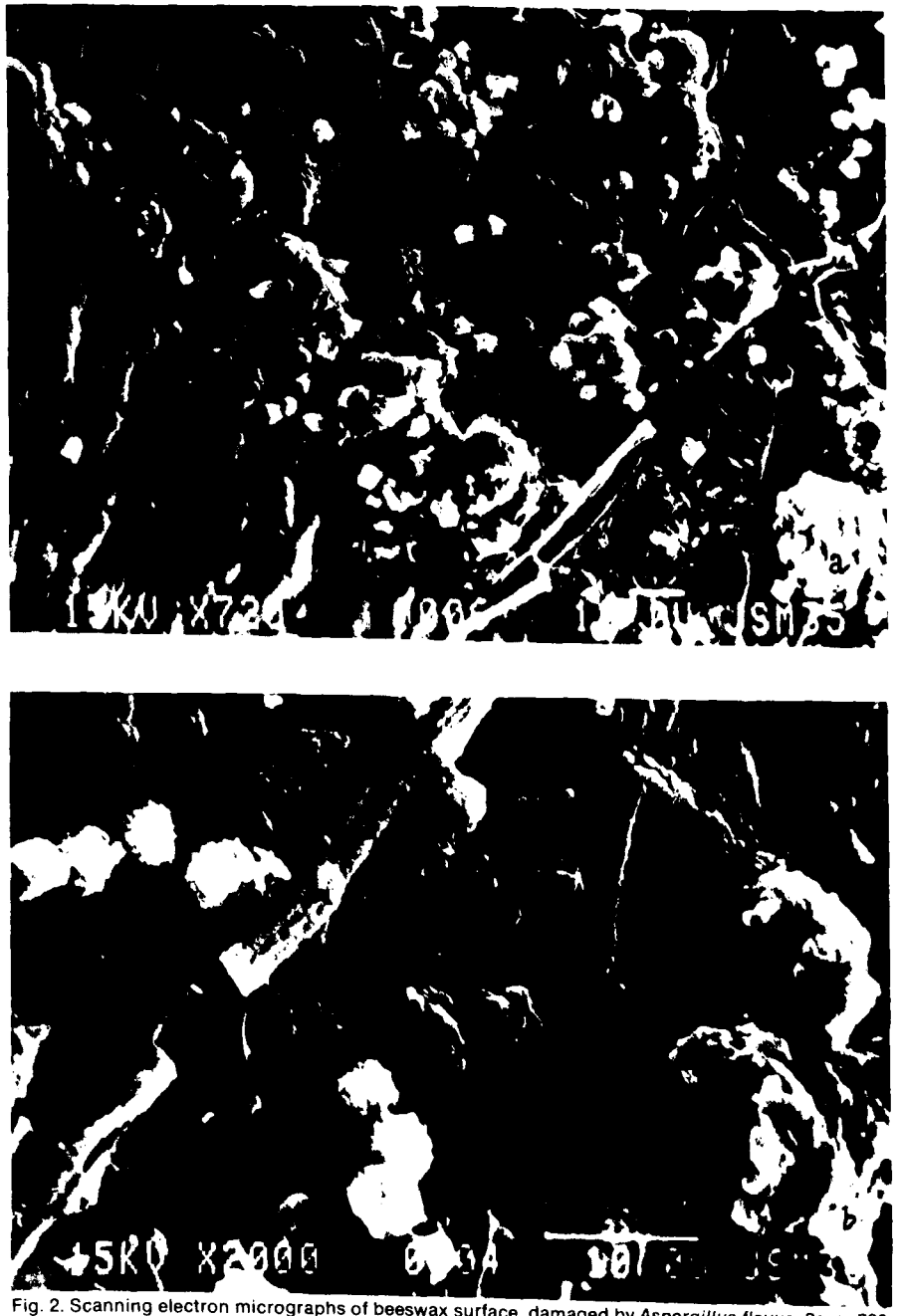

Fig. 2. Scanning electron micrographs of beeswax surface, damaged by *Aspergillus flavus*. 2a: × 720, 2b: × 2000.

Fig. 2. Microphotographies prises au microscope électronique à balayage de la surface de cire d'abeille endommagée par *Aspergillus Flavus*.

Abb. 2. Abtasten einer Bienenwachsfläche, die vom *Aspergillus flavus* zerstört ist, mittels elektronischer Mikrobilder.





seals began to be covered by a web of mycelium of *A. flavus* which in this case, almost, does not yield sporulation. The embossed lines on wax disappear and the wax loses its lustre, becomes glossy and whitish and begins to crumble. (Fig. 1,2) It is now possible to establish that during cultivation of *A. flavus* for three months, the beeswax loses over 20% of its original mass.

The fungus not only deteriorates materials, but it is also dangerous to the health of man.[8] This complicates work with materials attacked by the fungus and calls for special safety precautions. Special difficulties arise when protection against damage caused by *A. flavus* is effected using fungicides. This fungus has revealed a high staying power to the presence of doses of pentachlorophenolate (about 1%), salicil anilide (about 6%), polyhexamethylenguanidine (1.5%), benzalconiumchloride (1%), oxyquinoline (1.5%), and others, lethal for many fungi.

To prevent book destruction by this fungus, it is necessary to increase the doses of fungicides.


## Abstract

*Some Special Cases of Biological Deterioration of Books*

It is proved that owing to its high ecological adaptability, survivability and variety of fermentative complexes *Aspergillus flavus* Link is a widely distributed species of fungi. It deteriorates many materials of books including paraffined paper, paraffined calico tape, beeswax medieval seals and boards. The fungus is dangerous to the health of people as well. To prevent book deterioration by this fungus it is necessary to increase the doses of fungicides.



## Resume

*Quelques cas spéciaux de destruction biologique de livres*

Il est prouvé que, du fait de sa faculté d'adaptation écologique importante, de sa capacité de survie et de la variété de ses processus fermantatifs, l'Aspergillus Flavus Link est un type de moisissure très répandu qui contribue á la détérioration de nombreux matériaux de livres à l'inclusion des papiers paraffinés, des rubans calicot paraffinés, des sceaux et des cartonnages médiévaux à la cire d'abeille. Cette moisissure représente aussi un risque au niveau de la salubrité publique. Le traitement préventif des livres contre les effets de cette moisissure implique un accroissement des doses employées de fongicides.

RESÜMEE

*Einige spezielle Fälle der biologischen Verschlechterung des Zustandes von Büchern*

Es ist erwiesen, dass die Verbindung Aspergillus flavus aufgrund ihrer hohen ökologischen Anpassungsfähigkeit, Überlebensfähigkeit und Vielzahl an Fermentkomplexen eine weitverbreitete Pilzart ist. Diese verschlechtert viele Materialien, die für die Herstellung von Büchern verwendet werden, und zwar z.B. paraffiniertes Papier, paraffiniertes Kalikotape, mittelalterliche Siegel und Tafeln aus Bienenwachs. Dazu kommt, dass der Pilz auch für die Gesundheit des Menschen schädlich ist. Um zu verhindern, dass Bücher von diesem Pilz angegriffen werden, muss die Dosis der Fungizide erhöht werden.

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# Electron Microscopy of Parchment

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To provide optimal conditions for storing old manuscripts, it is important to know the causes leading to the destruction of parchment, the latter having served as the most wide-spread material for writing in the Middle Ages. It was manufactured of animal skins, mostly those of calves, goats and sheep. Physical properties of parchment mainly depend upon supramolecular collagen structures which are famous for their stability towards the influence of environmental factors. At the same time, changes in physico-mechanical and physico-chemical properties (mechanical strength, hydrothermic shrinkage, moisture absorbtion) of mediaeval parchment, even of that stored under favourable conditions, are well known. The present investigation was aimed at studying the ultrastructure of parchment and defining its submicroscopic changes which could be responsible for the lowering of mechanical strength.

## Materials and Methods

Samples of $11^{th}$–$19^{th}$ century parchments as well as those of modern parchment made of calfskin at the "Moskozhobyedinenie" enterprise for manuscript restoration have been studied. General characteristics of the samples are given in Table 1.

Fragments not larger than 1 sq.mm were fixed for 2 hours in 2% $OsO_4$ on 0.1M cacodylic buffer pH 7.3 and then dehydrated in ascending concentrations of ethanol. In addition, some samples were successively fixed with 3% glutaraldehyde on 0.1M phosphate buffer and 1% $OsO_4$ by Coulfield. In the process of dehydration the samples were treated with 3% uranium acetate (on the stage of 70% ethanol, 16 hours). To ensure a selective staining of proteoglycans, one part of the samples was fixed in the solution of $OsO_4$ with addition of ruthenium red of 0.0005% concentration. The dehydrated samples were embedded in Araldite. The ultrathin sections were stained with 30% aqueous phosphotungsten acid and with lead citrate by Reinolds and examined with an JEM-100S electron microscope at an accelerating voltage of 80kv.

## Results

The sample of modern parchment presented a leaf with a rather smooth surface consisting of closely packed collagen fibrils immersed in interfibrillar amorphous substance of moderate electron density. The collagen fibrils are straight,

Restaurator 5. 183–190 

Table 1. Samples under research and their Macroscopic Characteristic

Table 1. Echantillons faisant l'objet de recherches et leurs caractéristiques macroscopiques.

Tabelle 1. Muster, die untersucht werden und deren makroskopische Eigenschaften.

| N of sample | Origin | Condition of samples |
|---|---|---|
| 1 | Modern manuscript | Excellent |
| 2 | Byzantine manuscript, 11th cent., f. 202 | Satisfactory |
| 3 | Byzantine manuscript, 11th cent., f. 203 | Bad: the page is heavily thinned, its wholeness damaged |
| 4 | Byzantine manuscript, 12th cent. | Bad: the page is heavily thinned and deformed |
| 5 | German manuscript, early 13th cent. | Good |
| 6 | German manuscript, 14th cent. | Satisfactory |
| 7 | Old Russian manuscript, Gospels, 14th–15th cent. | Bad: the fold is fragile, with pink pigmentation |
| 8 | West-European charter, 17th–18th cent. | Good |
| 9 | Torah, 18th–19th cent. | Good |

and actually form a solid mass in which collagen fibril fasciles turned in various directions are discernible.

At great magnifications, longitudinally sectioned fibrils showed distinct transverse striation with typical periods and subperiods (Fig. 1a). Levels of the periods of adjacent fibrils coincide infrequently. The thickness of fibrils was about 80–90nm. Transverse sections of fibrils are rounded. In some places the outlines of transverse sections, periods and, particularly, subperiods are indistinct.

In the samples fixed with the addition of ruthenium red the electron density





of interfibrillar component is higher than in preparations treated without ruthenium. The borders between fibrils as well as dark subperiods are more distinct (Fig. 1b).

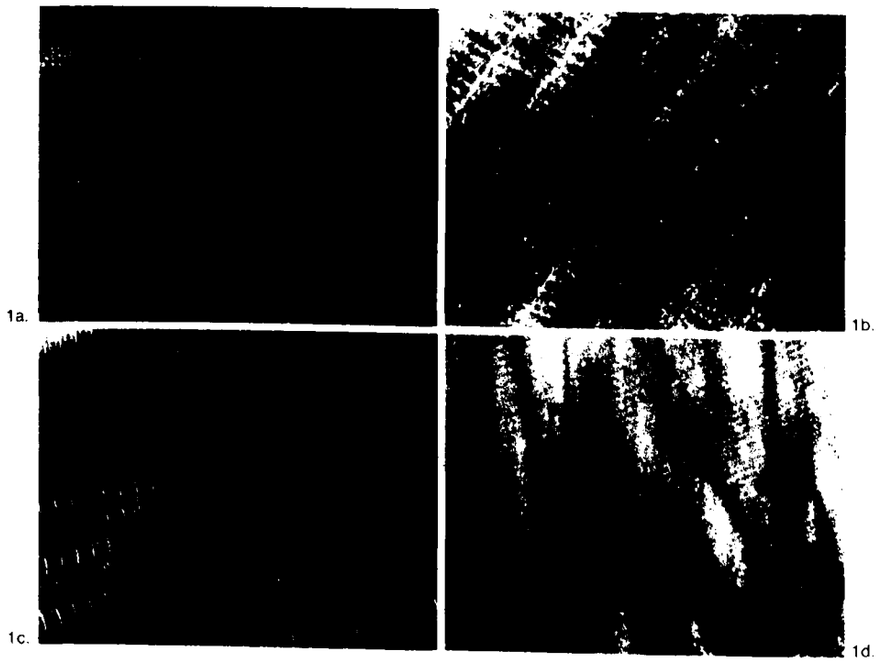
Well-preserved samples (5,8,9) of old-time parchments are close, as regards their ultrastructure, to the samples of modern parchment (Fig. 1c). But stronger roughness of page surfaces caused by protruding ends of collagen fibrils ("fraying") attracts attention. Slotlike cavities and those of irregular shape occurred between fibril fasciles in the thickness of a leaf. Not infrequently they communicate with the surface. In sample 8, streaks of amorphous material were found between collagen fibrils (Fig. 1d). On the surface of some samples there were, though not numerous, microorganisms which in some places did not come into direct contact with it.

The same structure is observed in satisfactorily preserved samples (2,6), but in some places the collagen fibril fasciles diverge in such a way that some parts of ultrasections look as if they were formed by isolated "islands" of collagen fibrils fasciles (sample 2). But for the most part, cracks spreading from the surface into the thickness of a page are observed (Fig. 2a). The surface of parchment is in some places smooth but mostly it is fringy. In sample 6 we found a colony of microfungi where cells with cellular wall, cytoplasmatic membrane, nucleus and nuclear membrane could be observed (Fig. 2b). The cells are heavily deformed, intercellular spaces in the colony are filled with amorphous material of moderate electron density. Rare microorganisms were sometimes seen on the surface of samples and inside the slots.

Longitudinally sectioned collagen fibrils in well and satisfactorily preserved samples show a typical periodicity, with distinct subperiods, particularly after treatment with ruthenium red. Nevertheless, parts, where periodicity of fibrils manifests itself weakly, occur here more often than in modern parchment. Interfibrillar amorphous material in the surface layers of a page shows a pronounced rhuteniophilia which decreases either sharply or gradually while deepening into the thickness of the parchment. In some places the abundance of rhuteniophilic substance shades the periodicity of fibrils.

In badly preserved samples (3,4,7) parchment looks in ultrasections as if it consisted of fragments with very irregular surfaces. In some cases it represents an unbroken page but having a strongly "eaten up" surface and numerous small and large cracks and cavities. Lots of microorganisms of rounded and polymorphic shape are deposited on the eroded surface and in slots. Many of them retain only a cellular wall and plasma membrane. Microorganisms tend to gather in chains inside slots, but on eroded surfaces and in large cavities in the thickness of a page they form irregular clusters (Fig. 2c and 2d).

Here and there accumulations of amorphous material, as well as collagen




Collagen fibrils of parchment

Fig. 1a. Transverse strokes in fibrils of modern parchment, × 63000. Fig. 1b. Fibrils of modern parchment after being fixed with addition of red ruthenium; rhuteniophil dark stripes are seen distinctly, × 61800. Fig. 1c. A well preserved 13th c. parchment, periods with 10–12 subperiods are seen distinctly, × 55900. Fig. 1d. Rhuteniophil amorphous material between collagen fibrils (arrows), × 20800.

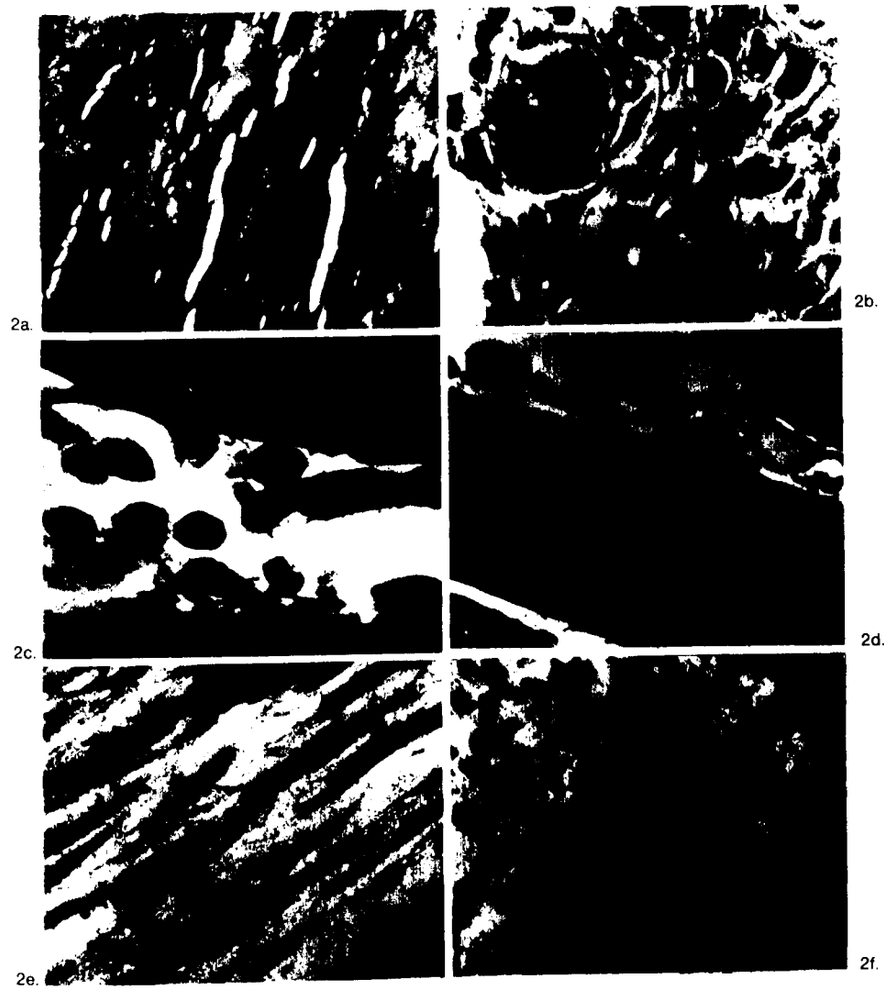
Fibrilles de collagène du parchemin

Fig. 1a. Structures transversales de fibrilles de parchemin moderne, grossissement × 63000. Fig. 1b. Fibrilles de parchemin moderne après fixation par addition de ruthénium rouge; les bandes sombres ruthénophiliques apparaissent nettement, grossissement × 61800. Fig. 1c. Parchemin bien conservé du 13ème siècle. Des séquences comportant 10 à 12 sous-séquences apparaissent nettement, grossissement × 55900. Fig. 1d. Présence de matière amorphe ruthénophilique entre les fibrilles de collagène (arcs), grossissement × 20800.

Kollagen-Fasern von Pergament

Abb. 1a. Quer verlaufende Linien in Fasern modernen Pergaments, × 63000. Abb. 1b. Fasern modernen Pergaments nach der Fixierung durch Zusatz von rotem Rhutenium; die dunklen Rhutenium-Streifen sind deutlich sichtbar, × 61800. Abb. 1c. Ein gut erhaltenens Pergamentstück aus dem 13. Jahrhundert, Perioden mit 10–12 Subperioden sind deutlich sichtbar, × 55900. Abb. 1d. Rhuteniophiles amorphes Material zwischen den Kollagen-Fasen (Pfeile), × 20800.






Destruction of parchment

Fig. 2a. Cracks between collagen fibril fasciles on a satisfactorily preserved part of parchment, × 10100. Fig. 2b. A part of colony of microfungi, × 9800. Fig. 2c. Bacteria in a crack between fibril fasciles, × 20800. Fig. 2d. A chain of bacteria on an eroded part of parchment; some bacterial cells are devoid of cytoplasm and nucleoid, × 11000. Fig. 2e. longitudinally sectioned decaying collagen fibrils, × 33800. Fig. 2f. star-like transverse sections of decaying fibrils, × 24700.

Destruction du parchemin

Fig. 2a. Crevasses situées entre les fasciles de fibrilles de collagène d'une partie de parchemin de conservation satisfaisante, grossissement × 10100. Fig. 2b. Partie d'une colonie de microchampignons, grossissement × 9800. Fig. 2c. Bactéries situées dans une crevasse entre des fasciles de fibrilles, grossissement × 20800. Fig. 2d. Chaîne de bactéries sur une partie érodée de parchemin, certaines cellules bactériennes sont dépourvues de cytoplasme et de nucléotides, grossissement × 11000. Fig. 2e. Fibrilles altérées de collagène, grossissement × 33800. Fig. 2f. Sections transversales en étoile de fibrilles altérées grossissement × 24700.

Zerstörung von Pergament

Abb. 2a. Risse in den Kollagen-Faser-Bündeln eines gut erhaltenen Pergamentteils, × 10100. Abb. 2b. Teil eines Colony eines Mikropilzes, × 9800. Abb. 2c. Bakterien in einer Spalte in Faser-Bündeln, × 20800. Abb. 2d. Bakterienkette in einem zerfressenen Pergamentteil; einige Bakterienzellen sind frei von Zytoplasma und Nukleoid, × 11000. Abb. 2e. der Länge nach geteilte, zerfallende Kollagen-Fasern, × 33800. Abb. 2f. sternförmig querverlaufende Teile von zerfallende Fasern, × 24700.

fibrils on different stages of degradation, were observed next to the colonies of microorganisms. The decay of fibrils takes place in the stage of microfibrillar splitting. Microfibrils are clearly seen on longitudinal sections of decaying collagen fibrils (Fig. 2e). Transverse sections of fibrils are of star-like or irregular shape (Fig. 2f). Places where fibrils have distinct periods and subperiods are seldom observed in the samples of badly preserved parchment. Significant parts of parchment consist of fragments of collagen fibrils alternating with microorganisms and flakes of amorphous material.

## Discussion

Methods of treatment of preparations for electron microscopy of human and animal connective tissue have proved to be quite suitable for samples of modern and old parchments. In all samples more or less distinct striation on collagen fibrils with subperiods can be variously observed. Fibrils in collagen fasciles are situated closer in parchment than in preparations of animal dermis (1–7). Efforts to identify in parchment samples either elastic fibres, cellular elements and their remnants or remnants of epidermis, blood-vessels, hair follicules, sweat- or sebaceous glands have failed.

A typical ultrastructure of collagen fibrils was observed in the samples of both old and modern parchment with the exception of heavily damaged parchment of the 11th c. Byzantine manuscript. In most cases, visual definition of the parchment condition coincided with that observed in the electron microscope.

All samples of parchments contained some rhuteniophilic material, its amount varying significantly in different places of the same preparation. This material is closely connected with collagen fibrils and forms, on their surface, something similar to belts repeating themselves with periodicity characteristic for collagen fibrils. Rhuteniophilic material is also present in the amorphous interfibrillar component of parchment.

The data found by us indicate that supramolecular collagen structures are of greater stability in the course of time. In some samples of old manuscripts, longitudinally sectioned collagen fibrils manifested an ultrastructure, characteristic for undamaged fibrils. However, various destructive changes could be observed in other samples of the parchment of old manuscripts.

We noticed two types of parchment changes. Change I is represented by cracks. We could not find out why they had emerged. It may be supposed that the cracks could appear in overdried samples. Change II is the forming of irregular cavities in the thickness of parchment as a result of lytic activity of microorganisms among which we noticed bacteria and microfungi (only in one





of the samples). A significant deformation of cells and absence of cytoplasm and nucleoid in some of them indicate that these cells are most probably not viable. It is close to the accumulations of microorganisms situated in the thickness of badly preserved parchment that small foci of collagen fibril decay are revealed. Judging by appearance of longitudinally and transversely sectioned degrading fibrils, their microfibrillar splitting precedes lysis of fibrils. We have never seen this in the samples which do not contain microorganisms.

In most cases both types of parchment changes, i.e. forming of cracks and fibril decay in the presence of microorganisms, accompany one another. However, there are samples which have only cracks but no accumulation of microorganisms in the thickness of parchment. It is possible that the forming of cracks precedes and promotes the penetration of bacteria.

## Conclusion

Electron microscopy of the samples of 11th–19th century parchment compared with a similar investigation of modern parchment gave an opportunity to reveal two types of changes, viz, forming of cracks between collagen fibril fasciles and decay of collagen fibrils as a result of lytic activity of microorganisms. The data obtained give an opportunity to suppose that forming of cracks precedes the penetration of microoorganisms into the thickness of parchment, thus promoting its destruction.


## Abstract

*Electron Microscopy of Parchment*

An investigation of ultrastructure of 11th–14th c. parchments (on various grades of preservation) in comparison with modern parchment has been carried on and showed that parchment consists of closely packed collagen fibril fasciles with typical periods and subperiods. Fibrils are cemented by amorphous interfibrillar (apparently, of protein nature) material containing rhuteniophilic compounds as well. In parchment samples which have undergone apparent changes two following ones have been found: forming of cracks between fibril fasciles and decay of fibrils as a result of lytic activity of microorganisms. The forming of cracks, most probably, promotes the penetration of microorganisms into the thickness of parchment, thus destroying it.



## Resume

*Microscopie électronique du parchemin*

Une recherche minutieuse de l'ultrastructure de parchemins datant du 11ème au 14ème siècle (présentant divers états de conservation) comparée à du parchemin moderne a été entreprise et montre que le parchemin consiste en un réseau dense de fibrilles de collagène avec des séquences

primaires et secondaires. Les fibrilles sont liées par un matériau amorphe interfibrilaire (de nature protéique apparamment) contenant aussi des composés rhuteniophiliques. Les échantillons de parchemin ont subi deux types de modifications successives visibles, à savoir la formation de crevasses entre les fasciles de fibrille et dégradation des fibrilles du fait de l'action lytique des microorganismes. La formation des crevasses favorise vraisemblablement la pénétration des micro-organismes dans l'épaisseur du parchemin conduisant à sa destruction.


## Resümee

*Elektronenmikroskopie von Pergament*

Eine Untersuchung der Ultrastruktur von Pergamenten des 11.–14. Jahrhunderts ( in unterschiedlichen Graden der Erhaltung) ist durchgeführt und mit modernem Pergament verglichen worden. Dabei hat sich gezeigt, dass das Pergmanet aus dicht gepressten Kollagen-Faser-Bündeln mit typischen Perioden und Subperioden besteht. Die Fasern sind mittels amorphen interfibrillen Bestandteilen (mit offensichtlicher Protein-Beschaffenheit) verbunden, die auch rhuteniophile Verbindungen enthalten. In den Pergamentmustern, die offensichtlich Veränderungen unterworfen waren, sind die beiden folgende gefunden worden: Bildung von Rissen in den Faser-Bündeln und Auflösung der Bündel aufgrund der Aktivität von Mikroorganismen. Die Bildung von Rissen fördert höchstwahrscheinlich das Eindringen von Mikroorganismen in den dichtesten Teil des Pergaments, wodurch dieses zerstört wird.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# Historical Survey of Research at the National Bureau of Standards on Materials for Archival Records[1,2]

*by* WILLIAM K. WILSON AND EDWIN J. PARKS

## Contents



1. A contribution of the Preservation Services Division of National Archives and Records Service (NARS), Washington, D. C. 20408, U.S.A., and Chemical Stability and Corrosion Division of the National Bureau of Standards, Washington, D.C. 20234, U.S.A.
2. Dr. Richard D. Smith, President, Wei T'o Associates, Inc., plans to review NBS work on the stability of leather in "The Deterioration and Preservation of Leather Bookbindings from Sulfuric Acid Attack". This is scheduled for publication in 1984 by Restaurator.

Restaurator 5: 191–241 

## 1. Introduction

The history of research on conservation and stability of records materials at the National Bureau of Standards (NBS) spans more than half a century, and research on the stability of materials related to records is still in progress. As the number of materials used in the generation of records, and in their conservation, has expanded, so has the number of problems. Our knowledge of polymer degradation mechanisms has greatly increased, allowing us to better cope with these problems, but stability of materials has been found to be far less simple than envisioned in 1925.

The definitions of the National Conservation Advisory Council[E-1]* are followed here, where conservation is a general term that includes preservation and restoration. Preservation includes security and environmental factors such as temperature, light, humidity and atmospheric pollutants. Restoration includes techniques of repair such as lamination, encapsulation, repairing tears in paper, etc. Not included in the definition of conservation, but of great importance to it, is the stability of materials that are used in the generation of records. This is the area in which NBS has made the greatest contributions.

Most of the work on stability and conservation of records was performed in the Paper Section and the Photographic Technology Section. These sections were created ca. 1921. The Paper Section ceased to exist as an organizational unit in 1975, although research on paper is still in progress in the Polymer Division. The Photographic Technology Section, later named Image Optics and Photography, ceased to exist ca. 1973, but the work is continuing in the Radiometry Division. Work on stability of polymers is currently in progress in the Polymers Division.

From the monthly reports of the Paper Section[1] it appears that stability of paper as a problem and potential area of research surfaced (ca.) 1925. Mr. Gösta Hall, of the Royal Technical University of Sweden, spent the month of June, 1925 in the Paper Section, and he had just completed a special study for the Government Testing Institute in Sweden on the permanence and durability of paper. Mr. Hall was of great assistance to NBS scientists, and he influenced the direction of research on stability of paper for many years to come. Mr. Hall suggested that acidity derived from alum used in the sizing of paper played an important part in stability, and a variation of a method for determining titratable acidity in paper is a standard TAPPI method today[E-2]. He also developed the dry accelerated aging method that still is a TAPPI standard[E-3], and recent

* Letters and numbers refer to references in Section 5.

1. On file at National Archives and Records Service.





work shows a correlation between his accelerated aging procedure and natural aging[A-72]. (Recent publications by Graminski, *et al.*[A-70] indicate that an accelerated aging procedure should contain some moisture).

Representatives of the paper industry suggested in 1926 that NBS should evaluate a special purified wood fiber in comparison with rag fiber as a papermaking raw material, and a research associate entered on duty February, 1928 for this purpose. In October, 1928, a research associate of the Rag Content Manufacturer's Association came to the Paper Section to work on the permanence of fine writing papers. In 1929 the active cooperation of D. A. Clibbens, British Cotton Industry Research Association, was reported.[1]

In August, 1927, a representative of the New York Public Library and a representative of the paper industry visited NBS, having been cleared with the Secretary of Commerce (parent agency of NBS), concerning potential research at NBS on conservation and stability of records. This research program materialized a year later with the cooperation of the American Library Association and with funds provided by the Carnegie Foundation through the National Research Council.

In April, 1929,[2] the following research program was outlined: "(1) tests of the current commercial rag fiber and wood fiber products including the fibrous raw materials, (2) tests of similar papers made in the Bureau paper mill and therefore having a definitely known history, (3) inspection and testing of papers of known age, (4) a study of means of overcoming influences found to be harmful to the life of papers, and (5) research to find the nature of the reaction of paper celluloses to deteriorating influences".

In ca. 1920, NBS acquired an experimental paper machine with about a 30-inch trim, which probably was unique in the U.S.A. at that time. This enabled the manufacture of paper under typical mill conditions, from beating of pulp through to the finished paper, with known characteristics, for both immediate testing and setting aside of samples for study of the effects of natural aging. Due to organizational and personnel changes over the years, the conservation of samples for natural aging was only partially successful.

In 1939 Scribner[C-7] reported on the results of the research program as follows:

"Active research on problems relating to the preservation of records has been in progress in the paper section of the National Bureau of Standards since 1929. This work has dealt with the properties of papers and photographic films with particular reference to their stability and strength, and with means of

2. Monthly report of the Paper Section, NBS.

minimizing extraneous deteriorative influences during the storage and use of these materials.

"The work has been conducted with the assistance of an advisory committee appointed by the National Research Council, and representative of library, archival, and manufacturing interests. In addition to funds of the National Government, the Bureau has received the financial assistance of the Carnegie Foundation of New York, and of manufacturers of the materials.

"The research related to the preservation of records contained on paper resulted in a recommended classification and specification of papers for the various classes of records, in information which assists the papermaker in choosing his raw materials and making the best use of them in manufacturing record papers, and in recommended storage conditions for their preservation. The results of this work are summarized in a report (Miscellaneous Publication M154) similar to this one.[A-24]

"Research on the use of photographic films was undertaken in 1935. For this work, in addition to funds from the Carnegie Foundation, the Bureau's funds have been supplemented by those of three other Government organizations – The National Archives, the Department of Agriculture, and the Social Security Board – and by a fund depositied with the National Research Council by several manufacturers of photographic films and equipment. Also, helpful advisory assistance was given by a committee representative of these interests".

This somewhat tortuous introduction to the beginnings of research on record materials at NBS shows the following: (1) the need was genuine; (2) the interest was high level; (3) cooperation was international; (4) with the exception of the work in Sweden, a vacuum existed with respect to organized research in this area; (5) outside financial support of records research catalyzed the channeling of some NBS funds into this area; and (6) many U.S. Government and State agencies and the paper industry were interested. It is obvious that the need has been great, or financial support would not have been available, albeit intermittently, for over 50 years.

Determination of the properties of materials was included in the Act of March 3, 1901 establishing the National Bureau of Standards[E-4], and the Act directed NBS to " . . . exercise its functions for the Government of the United States . . ." As interest in the stability of record materials extends far beyond this central continuing mission of NBS, most of this research has been supported by other agencies.

There has been a marked change over the past 20 years from sponsored research by records institutions to in-house research.





## 2. Description of work in relation to technical areas

### *2.1 Accelerated Aging*

In order to predict the stability of any given material, it is necessary to develop a meaningful accelerated aging procedure for this material. To do this, one must develop information on the environmental conditions that promote degradation, the specific chemical entities (functional groups, impurities, manufacturing details) that lead to instability, and the mechanisms of degradation. The end product for the archives and libraries is a specification that describes a stable material for the generation or conservation of records.

The stability of materials to be used at ambient temperatures presents a unique problem in polymer degradation studies. An extensive body of literature exists on the thermal stability of polymers[E-5,6,7], but most of these papers describe pyrolytic degradations at elevated temperatures. Accelerated aging procedures are needed that take into account the chemistry of the material in relation to the service and storage environment. Accelerated aging procedures usually, but not always, have included an elevated temperature, high enough to increase the rates of reactions that occur at room temperature, but supposedly not high enough to initiate other pyrolytic reactions. There have been many exceptions in which elevated temperatures were not applicable. Examples are the stress-cracking of rubber by ozone at room temperature[E-6], (p. 261), and the enhanced degradation of cellulose by the catalytic oxidation of sorbed sulfur dioxide to sulfur trioxide by certain metals[E-8, A-4]. In these situations, stress accelerated aging conditions are imposed without an elevated temperature. It is obvious that accelerated aging requires consideration of the chemistry of the materials and situations involved.

The first accelerated aging method for paper was developed by Gösta Hall of Sweden[E-9], and the procedure used by NBS (72 h at 100°C in a circulating oven) was derived from Hall's work. Hall attributed the degradation of paper principally to the presence of alum used in rosin sizing. The use of alum does produce an acid situation in paper, but not necessarily from the hydrolysis of aluminum sulfate, as popularly believed (but not stated by Hall). Launer showed that aluminum was selectively sorbed from alum solution by paper pulp, but sulfate was not selectively sorbed[A-30]. This is an ion-exchange reaction. In addition, both aluminum and acid produce crosslinking in paper[E-10], and crosslinking produces changes in the physical properties of paper similar to changes produced by hydrolysis.

Thus, the net results of dry accelerated aging, i.e. degradation of properties of paper, has a somewhat broader explanation today. The real test of an accelerated aging method, however, is how well it correlates with natural aging.

Although the concept of this comparison is simple, execution is difficult, and only a few such comparisons have been reported. Two such comparisons have been made by NBS[A-47,72]. Very few organizations can maintain the continuity necessary to complete a project that spans 25–50 years, especially when there is no pot of real gold at the end of the trail. And as science marches on during this long period of waiting, one may find that comparisons are based on analytical procedures that do not tell the same story told by the obsolete methods of 50 years earlier.

The first comparison of accelerated aging (72 h at 100°C) with natural aging was started in 1928[A-1]. A group of commercial papers was tested before and after accelerated aging, and samples of these papers were retested after four[A-17], eight[A-32] and 26 years.[A-47] After 26 years it was concluded that a "fair" correlation existed between natural and accelerated aging. It was also concluded that: "While this is qualitatively a valuable conclusion, no quantitative conclusions can be drawn from this experiment since the manufacture and testing of paper had not progressed far enough in the late twenties to permit the proper control of variables in the selection of samples, and since the relation between accelerated aging and natural aging is, in all likelihood, a function of these variables".

A far more meaningful comparison between accelerated aging and natural aging was made with a group of 18 book papers made on the small paper machine at NBS in 1937[A-29]. Although originally there was no plan to test these papers after a period of natural aging, they were representative of a larger group retained for several years for other purposes. As their manufacturing history was known and the papers had been extensively evaluated for the time of manufacture, these 18 papers were assembled into a reasonably coherent set of samples[A-72]. Three fiber compositions were available in this set of papers: 50–50 soda-sulfite, purified wood pulp, and old rag. The soda-sulfite papers contained a high percentage of hemicelluloses (measured as pentosans), the purified sulfites a low percentage of hemicellulose, and the rag papers none.

Keeping in mind the limitations of accelerated aging procedures, the following inferences may be drawn from the data in this report:

(1) The changes in alpha cellulose that occurred during accelerated aging for three days at 100°C correlated well with changes in alpha cellulose that occurred after 36 years of natural aging. Retention of high alpha cellulose content, or perhaps some more convenient alkali solubility method, should be suitable as a criterion of resistance to accelerated aging.
(2) Changes in copper number that occurred during accelerated aging for three days at 100°C correlated well with changes in copper number that occurred after 36 years of natural aging.





(3) Correlations of retention of folding endurance after natural and accelerated aging only were fair! Although fold is useful as an evaluation method after accelerated aging, one should not rely on it completely.
(4) Correlations of internal tear between natural and after accelerated aging were somewhat better than for folding endurance, but still not high.
(5) Correlations between cold extract pH in 1937 and changes after natural aging in alpha cellulose, copper number, fold, tear, and elongation indicate that pH is a reasonably good criterion of stability, possibly for complex reasons.
(6) pH, and changes in alkali solubility, reducing power and tearing strength after accelerated aging for 72 h at 100°C are reasonable indications of stability. Fold is sensitive to accelerated aging, but not as useful an indicator.
(7) Data obtained after natural aging indicate that zero span tensile, elongation, and strength when wet as a percent of strength when dry are useful criteria.
(8) When data in this report are compared with data obtained from hand sheets at 90°C and 0% and 50% R.H., it appears that an accelerated aging atmosphere should contain some moisture, but not as much as 50% R.H. at 90°C.

Prediction of the permanence of paper from accelerated aging data is not an exact science, but several investigators have directed their efforts toward this goal[E-11]. The usual approach is to determine the rates of degradation of some property at several temperatures and apply some form of the Arrhenius equation to an evaluation of the data. This presumes that plotting a function of degradation during accelerated aging against the reciprocal of the absolute temperature gives a straight line. This implies that the same reaction occurs over the temperature range in question. As one can write down ca. 20 variations of the anhydroglucose ring in cellulose, the likelihood of this happening for a broad spectrum of papers on an Arrhenius plot is somewhat remote. Another factor is that the breaking of only 1 or 2% of the bonds between the anhydroglucose units in the cellulose in a paper can render the paper useless. Thus, a physical property (fold, tear) might be reduced from full value to zero through breaking one or two bonds per 100 bonds in the paper. It is no wonder that the data from tests that are a function of molecular weight and molecular weight distribution frequently are so variable. And we have not mentioned the contribution of sheet formation to physical properties.

In spite of the complexities, and in view of the need, the authors feel that accelerated aging can be useful under the following conditions:

(1) For ranking the stability of papers in a group relative to each other.
(2) For comparing papers that are similar in composition and manufacturing history.
(3) For estimating rough categories of permanence in years: up to 50 years; 50–100 years; or several hundred years. This is done in the four ASTM specifications for permanent records[E-12].
(4) Provided that more than one test is used in evaluating changes in paper after accelerated aging, and the tests are related, if possible, to the end use of the product.
(5) Provided some moisture is included in the aging atmosphere, as discussed below.

As part of the long-range research program for NARS 1966–1978, an extensive evaluation of the stability of laboratory handsheets was carried out[B-13,14,15]. The attitude was taken that testing of commercial papers, while valuable for some purposes, was of limited utility for evaluating parameters of importance in the stability of paper.

One of the parameters of interest was the metal salt of the cellulose carboxyls. Sihtola[E-13]has shown that the metal on the No. 6 carboxyl in cellulose can have a great effect on yellowing during accelerated aging. The same effect was also observed for dicarboxyl oxycellulose[E-14,15]. For this reason, it was concluded that an investigation of aluminum, a metal that might become attached to the carboxyls during sizing, would be of interest.

The effects of moisture and of oxygen were determined qualitatively by carrying out accelerated aging procedures at 90°C in (1) dry air, (2) dry nitrogen, (3) moist air (50% R.H.), and (4) moist nitrogen. The changes in dry air and dry nitrogen usually were negligible to moderate, depending on the property measured.

Samples treated with aluminum ion proved to be unstable during accelerated aging at 90°C, and handsheets made from the deashed modification (metals completely removed by several treatments with acid) proved equally unstable. Handsheets made from the unmodified pulp were comparatively stable.

A reversal of the effect of moisture was noted in wet breaking load as a function of dry breaking load. Although this property increased with time of aging for both moist and dry aging, the effect was far more pronounced for dry aging. In addition, wet breaking load as a percent of dry breaking load went through a maximum during moist aging, but continued to rise during dry aging. It would appear from this that crosslinking occurs during both moist and dry aging, but a competing reaction tends to destroy crosslinks formed during moist aging[A-72].





Moisture regain presents an interesting contrast to wet breaking load. Although moisture regain decreases slightly during dry aging, the decrease during moist aging is pronounced. One would expect moisture regain to decrease during crosslinking, but apparently there is little or no association. It would appear that the decrease in moisture regain during moist aging is due to an increase in crystallinity[E-16,17(b)] (pp. 38, 996).

Moist aging was devastating to blue reflectance, internal tearing resistance, folding endurance and load at break. As expected, the changes in properties are more pronounced in moist air than in moist nitrogen, but substantial change occurred in moist nitrogen[A-27]. Considerable change occurred in acidity as measured by the hydrogen ion concentration of the paper extracts. Changes in moist nitrogen were about one third to one half of the magnitude of the changes in moist air.

Graminski[A-70] made a systematic study of the effects of temperature and moisture on the accelerated aging of paper using handsheets made from deashed (metal-free) pulp. The temperatures studied ranged from 60° to 90°C, and the R.H. from 0% to 90%. Graminski concluded that degradation rate of paper at elevated temperature is dependent on the amount of water bound to the cellulose, and that a fraction of the bound water is inactive. Although he did not conclude that paper degradation is a function of moisture content, preferring to use the term "bound water", calculation of activation energies from plots of degradation rates against moisture content gives values that are consistent with the degradation reactions that might be expected in cellulose.

The data of Graminski[A-70] and earlier data by Parks[B-13,14,15], some of which was recalculated to different forms[A-27], were used to select conditions for accelerated aging of paper in a moist atmosphere. A procedure for accelerated aging at 90°C and 25% R.H. has been prepared and approved by Subcommittee 2, Testing Methods and Quality Specifications for Paper and Paperboard, which operates under Technical Committee 6, Pulp, Paper and Paperboard of the International Standards Organization. Any accelerated aging procedure is a compromise, because all of the information needed to write an accelerated aging procedure is never available. The available information from Parks and Graminski indicates that *some* moisture should be present in an accelerated aging procedure for paper, but that 50% R.H. was too much. 25% was taken as a compromise.

### *2.2 An Analysis of the Aging of Paper*

Wilson[A-71] has reviewed the various chemical and physical changes that might occur in paper and the probable effects of these changes on measurable proper-

ties of paper. Among the changes that might occur in cellulose and paper are hydrolysis, oxidation, crosslinking, changes in lateral order and, under some conditions, thermal decomposition. These changes will result in changes in chemical and physical properties of paper, and the kinds of changes will be dependent to some extent on the starting material. Photolysis of a paper made from "pure" cotton fiber would cause some chain scission and a little yellowing (in air) with a very low quantum yield. Photolysis of newsprint would cause considerable chain scission and massive yellowing with a much higher quantum yield.

Crosslinking in cellulose has been recognized for many years as a procedure for stiffening fiberboard with acid and certain metal salts[E-10,18,19]. Apparently Graminski was one of the first to recognize that crosslinking might be one of the factors in the natural aging of paper[A-62]. This was not recognized earlier, as both crosslinking and hydrolysis result in a decrease in folding endurance, the principal test to measure deterioration in paper.

The following tests should be useful in determining *what* happens during the aging of paper[A-71]:

(a) Zero-span tensile (fibre strength)
(b) Wet tensile as a percent of dry tensile (crosslinking)
(c) pH (generation of acid)
(d) Alkali solubility (chain scission and alkali sensitivity)
(e) Functional group content (oxidation and hydrolysis)
(f) Molecular chain length distribution (chain scission and randomness of chain scission).

The following tests should be useful for *detecting* changes during the aging of paper, but are not particularly useful for *identifying* the chemical and physical processes involved in the change:

(a) Folding endurance
(b) Tearing strength
(c) Elongation
(d) Tensile energy absorption
(e) Alkali solubility (in this group if no other information is available)
(f) Copper number
(g) Viscosity

Several specific situations related to the aging of paper deserve special attention, such as the catalytic action of metals, generation of acid from unsuspected sources, and the potential of air pollutants for causing damage to paper. These situations can only emphasize the fact that there is no substitute for developing as much information as possible on the chemistry of the paper under study. Metals are especially troublesome as they can cause yellowing, promote crosslinking, and catalyze the oxidation of sulfur dioxide to sulfur trioxide. With the exception of sulfur dioxide, little is known about the effect of air pollutants on paper. Presumably ozone is not a factor as it only attacks moist cellulose[E-20]. Oxides of nitrogen in the air are unknown factors in the degradation of paper.



### 2.3 Rag Paper vs. Wood Pulp Paper

Fifty years ago wood pulp papers did not enjoy the reputation for durability and permanence that rag papers enjoyed. One of the earliest research projects on permanence of paper was initiated to develop information on the permanence of wood pulp papers, and this required the refinement of the accelerated aging procedure introduced by Hall (mentioned in sections 1 and 2.1). Rasch[A-1,7] was able to make papers from highly purified wood pulp that had excellent strength properties, "exceeding the strength requirements of the highest-grade bond papers purchased by the U.S. Government Printing Office and . . . the strength requirements for United States Currency"[A-7].

Rasch confirmed the findings of Hall that the stability of rosin-sized papers was seriously impaired when excess alum was used. When the pH at the head box was maintained at a reasonably high level, a stable paper was produced. This is in keeping with the data obtained on some of the 36-years old papers. One of these papers was sized with rosin and only a small amount of alum, and the stability toward natural aging was outstanding.

Rasch also found that a surface size of glue appeared to improve stability. The glue, of course, acted as an acid acceptor and minimized the effect of the alum.

It is interesting that pH data are not reported in Rasch's first paper in 1929[A-1]. Titratable acidity, determined by titrating water extracts after heating for 1 h at 100°C, was used as a measure of acidity. For this reason, pH was first determined on such an extract, cooling to room temperature before measurement. This hot extraction method is still in use today[E-21]. Rasch determined pH using isohydric indicators and reported the data in his 1931 paper[A-7].

Rasch was able to show that permanent and durable papers could be made from purified wood pulp. Today most papermakers probably would agree that both rag papers and wood pulp papers cover the spectrum of permanence and

durability. In the market place it becomes a matter of choosing what is available, or specifying what is needed, and paying the price.

### *2.4 Relation of Ink to Stability of Records*

For hundreds of years writing inks contained ferrous sulfate, tannic acid and/or gallic acid and gum arabic. Many of these ink formulations from the colonial period also contained alum[E-22]. These inks were acid because the reactions in the inks themselves would produce more or less acid, and the alum, if present, would produce an acid state. Barrow[E-22,23] determined the pH values of inked areas and uninked areas of several old papers, and the values from the inked areas were substantially lower. It is not surprising that the inked areas in many old papers are badly deteriorated.

In 1935 NBS published a paper authored by Zimmerman entitled Relation of Ink to the Preservation of Written Records[A-21]. All of the inks studied contained an iron salt, and most of them contained sulfuric acid, hydrochloric acid or oxalic acid. The GPO standard at that time included 25g of dilute hydrochloric acid per liter. Two of the experimental inks studied by Zimmerman[A-21] were made from ammonium ammoniumoxyferrigallate, a compound first discovered by Silbermann and Ozordwitz (*oxy* in early German literature means *hydroxy*)[E-24,25].

Using the accelerated procedure developed by Rasch[A-5], Zimmerman determined the effect of these inks on several papers. The inks containing acid greatly accelerated deterioration. The ammonium ammoniumoxyferrigallate inks had very little effect.

This alkaline ink is somewhat difficult to make, especially in large quantites, but this problem was solved by Kantrowitz[E-25]. It was available from the Government Printing Office for many years.

A wealth of information on writing inks and several specialty inks for 1940 and earlier is contained in NBS Circular C426 by C. E. Waters, published in 1940.

A total revolution has occurred in writing inks and writing instruments in the past 40 years. The ball-point pen has taken over almost completely, with some competition from felt tips. Although not quite dead, the fountain pen essentially has joined the ranks of the quill and the steel dip-pen. Very few of the manuscripts prepared using iron gallate inks have entirely faded, but we have little information about what to expect from the modern ball-point pen. The operation of this pen essentially dictates the use of a dye instead of a pigment. No published data on the colorfastness of dyes used in ball-point pens have come to the attention of the authors.





A similar revolution in office copying technology has occurred within the same time frame as the ball-point pen. A revolution within a revolution has occurred within the past 10 years with the explosion of the huge variety of office copying machines, not to mention the evolution of typewriters from manual to electric to the sophisticated word processor. The emphasis on "quicker and cheaper" has left its mark in many places in the printing world. For example, one cannot hold many magazines with a thumb or finger on a printed area without smudging. The introduction of "erasable" typewriter paper and "correctable ribbons" are mixed blessings – streamlining of office procedures with the potential risk of less durable copy. For 99% of the needs of our society, the new technology is a blessing. It has created problems for those who need permanent and durable copy.

As part of the research program for NARS 1966–1978, a specification for copies from office copying machines was developed[E-12]. Requirements for the paper and for the durability and permanence of the copy were included, and one of the test procedures for durability of the "printing" included an abrasion test. The laboratory work for the development of this specification was performed in 1973 and the specification was promulgated by ASTM in 1975. When the specification came up for automatic review in 1980, the office copy field, the word processor, and other types of printing – all had changed so drastically that only practically obsolete types of "printing" passed the test. This problem has not yet been resolved, and it merits serious attention.

### *2.5 Analytical Methods*

The analytical methods available for the evaluation of cellulose and paper in 1930 are archaic by today's standards. This is understandable, for the concepts of polymer theory had not seeped very far out of university laboratories at that time. "Staudinger pioneered in the subject, and Carothers, Flory, Huggins, Mark, Meyer, and others surmounted many of the main obstacles in a series of brilliant studies beginning in the 1920's"[E-26]. The crystalline nature of cellulose apparently was first recognized by Nägeli in the last century[E-27], but his work was not accepted.

The development of the nature of cellulose from 1920–1950 paralleled the development of polymer chemistry and many investigators contributed to this development. Only a few highlights are mentioned. Herzog and Jancke recognized that cellulose from widely different sources had identical crystalline structures[E-28]. Meyer and Mark, and coworkers, did extensive work on the unit cell of cellulose[E-29,30,31,32]. Nickerson reported on the "leveling-off" rate of hydrolysis of cellulose[E-33], and the "leveling-off" degree of polymerization

during hydrolysis[E-34]. Howsmon [E-35] made substantial contributions to an understanding of the crystalline and amorphous nature of cellulose, and to changes in crystallinity that occur during hydrolysis.

In 1930 it was believed by many that the permanence of paper was a function of the purity of the cellulose from which it was made, and alpha cellulose and copper number were the tests most commonly used for the determination of purity. The alpha cellulose test is one of the many alkali solubility tests used for cellulose. All of these tests are empirical in nature, and the solubility depends in part on the strength of the sodium hydroxide solution used in the test. It was believed that unmodified cellulose was insoluble, but we now know that the short chain material dissolves and the solubility may or may not be a function of cellulose modification. Rasch modified and improved a gravimetric method, but made no provision for correcting for rosin, starch, glue or other materials that might be in paper. One of his principal contributions was the use of a grinder, designed by Gösta Hall, similar to the one used by the Swedish Government Testing Institute[A-1,9]. This grinder disintegrated the paper to a cotton-like material that was readily accessible to reagents.

Launer later modified the gravimetric method, to us a much smaller test specimen (0.3 g vs. 5.0 g), and determined the cellulose fractions by oxidation with dichromate. Correction factors were worked out for rosin, glue and starch[A-27,28].

Rasch also worked out the details of a procedure for the determination of copper number[A-9]. Copper number is a function of the reducing power of cellulosic materials with respect to alkaline copper solutions. Copper number has been a very useful determination, but it is empirical in nature. The relationship between copper number and carbonyl content as determined by a borohydride method is linear, but the value of the copper number/carbonyl content ratio was different for various types of modified celluloses[E-36]. Wilson and Padgett[A-46] used sodium chlorite solutions at pH 3.5 to oxidize aldoses and modified cellulose, and a procedure based on this oxidation was used to obtain approximate aldehyde values. Different aldoses reacted at greatly different rates, and different cellulose modifications also reacted at different rates. This approach can be used to obtain information on the various modifications of the anhydroglucose ring in cellulose.

Launer developed a procedure for the determination of pH of paper[A-31] and obtained information on the sorption of aluminum by cellulose which has a profound effect on pH[A-30]. Before the determination of pH, as noted in 2.3, acidity in paper was measured by titrating the hot water (cooled to room temperature) extract of paper under standard conditions. When procedures for the determination of the pH of paper extracts became available, it was natural





to start with this hot water extract. Launer took the position that heating was unnecessary, and developed a procedure based on extraction of 1 g of paper by 70 ml of water for 1h. Both hot and cold extracton procedures are TAPPI methods[E-2,21]

Differences exist between hot and cold extraction, and these differences are not always predictable. Usually, pH determined by a hot extraction procedure is lower than a pH value obtained by a cold extraction procedure. Launer attributed this to the hydrolysis of alum, and was able to show experimentally that this occurred. However, Launer also showed that aluminum was selectively retained by cellulose and, within the limits of the precision of the measurements, sulfate was not sorbed. Today we would attribute the sorption of aluminum to ion exchange with the carboxyl groups in cellulose.

Wet strength resins were introduced to the paper industry about 40 years ago. It was soon discovered that the difference in hot extraction pH and cold extraction pH was much less for papers containing melamine resin. If the paper contained large amounts of wet strength resin, hot extraction pH actually could be higher than cold extraction pH. Wilson, et al. made a systematic study of the effect of melamine resin on chemical tests of paper[A-39].

Flynn and Smith determined the pH values of a large group of papers by three different procedures: (1) TAPPI cold extraction, (2) spot test with water as the contact medium, and (3) spot test with 0.1 *N* KCl as the contact medium[A-52]. Although one could say from plots of cold extract pH against "water spot pH" that a correlation existed between the two methods, the data are too erratic to draw any solid conclusions.

Determination of the pH of paper by any method can lead only to empirical data. A pH test indicates the hydrogen ion activity of the extract of the paper specimen, but it does not give direct information on the hydrogen ion activity in the paper itself, and this probably varies with the moisture content. Wakeham and Skau approached this problem by measuring the pH of textile materials at several different ratios of fabric to water, and extrapolating the data to the amount of moisture the sample would contain at 21°C and 65% R.H. (standard testing atmosphere)[E-37]. Apparently this approach has never been used for paper.

Parks[B-21] demonstrated substantial differences in apparent pH readings depending on whether or not the paper test specimen made intimate contact with the electrodes of a pH meter. He recommended that pH be measured on decantates rather than on paper suspensions.

*2.6 Environmental Considerations*

One of the early tasks in research on the conservation of records at NBS was "to ascertain the kind and amount of equipment which libraries have available for the protection of records in their charge, and to get information about the visible effects of light, dust, dampness, and similar factors"[A-24]. The following is a summary of the findings:

(1) About one third of the libraries surveyed had equipment for removal of dust from air in the ventilation systems.
(2) About one third of the libraries surveyed could control the humidity.
(3) Light protection, in general, was excellent.
(4) Cleanliness and ventilation were well maintained and little difficulty was experienced with pests.

The original paper on which these conclusions were made was authored by Kimberly and Hicks[A-11].

Kimberly studied the effect on various papers of a few parts per million of sulfur dioxide in the laboratory at 30°C and 65% R.H.[A-13]. Exposure to sulfur dioxide for 10 days caused large increases in acidity, but only nominal changes in folding endurance, copper number and alpha cellulose. This is to be expected, for 10 days is hardly enough to cause substantial degradation, although it is long enough to obtain sorption of sulfur dioxide and increase the acid content of the paper. If the papers had been allowed to age naturally for several months, the results might have been different.

Hudson has done some excellent work on the sorption of sulfur dioxide by paper[E-38].

Kimberly and Emley[A-14] conducted an extensive testing program of books in various city and county libraries in the U.S. in order to check the effect of air pollution on deterioration of paper. This was probably the first *reported* project of this type to obtain quantitative data on this problem. Through the cooperation of several libraries, identical books from these libraries were analyzed for acid content, alpha cellulose, copper number, folding endurance and fiber content. The following conclusions were drawn from this work:

(1) The paper in books in relatively unpolluted areas was always in better condition than paper in books stored in polluted urban areas.
(2) The greater deterioration of books stored in large cities was attributed to air pollution.





(3) Papers containing appreciable quantities of ground wood were in poorer condition than those containing rag and chemical wood.
(4) Papers of different quality sometimes were used in the same book.
(5) The acid contents of identical books stored in various libraries appeared to be a function of air pollution.
(6) The same was true for alpha cellulose and copper number. These two tests are very useful for indicating changes in cellulose.

Hudson[E-39] and Smith[E-40], in more recent studies, have shown experimentally that substantial differences exist in the condition of books in libraries in polluted and non-polluted areas. Jarrell[E-41] showed that the margins of old books and magazines were deteriorated more than the centers, and contained more acid. A book made from paper with an alkaline filler was not degraded, but the margins contained more water-soluble sulfates than the centers.

Kimberly and Emley investigated the removal of sulfur dioxide from library air[A-15] as the final step in the study of the effect of air pollution on paper. They found that an air washer using untreated water did not completely remove sulfur dioxide from library air. Sulfur dioxide was substantially eliminated by washing with water in which the pH was maintained in the range 8.5–9.0. The alkaline material, recommended by a supplier of air-conditioning equipment, contained the following ingredients: sodium silicate, sodium hydroxide, sodium carbonate, sodium dichromate and trisodium phosphate.

Jarrell, *et al.*,[E-42] studied the deterioration of paper in a gas chamber in which the burning of illuminating gas produced a consistent percentage of oxides of sulfur. His conclusions were similar to those of Kimberly[A-14]. Apparently Jarrell and his coworkers initiated their work on the effect of sulfur dioxide on paper before Kimberly, but their results were not published until 1936[E-41] and 1938[E-42].

Weber, *et al.*[A-20] studied the effects of various fumigants on paper, and concluded that fumigants caused no damage. Among the fumigants studied were hydrogen cyanide gas, ethylene chloride with carbon tetrachloride, carbon disulfied, ethylene oxide with carbon dioxide, and methyl formate with carbon dioxide.

In 1931 Wilkie published a report on an investigation of laundry "winter damage" which contains some valuable information that could be applied to paper, and apparently this report has been generally overlooked by the preservation community[A-4]. This report covers a study of damage to cotton fabrics that were allowed to dry outside in the New England winter, i.e. the damage occurred only in the winter and only in New England. It was determined that damage was a function of the high concentration of sulfur dioxide in the air

from the burning of fossil fuels, and that the oxidation of sulfur dioxide to sulfur trioxide was catalyzed by iron and possibly other metals. An alkaline rinse that included some calcium bicarbonate, formed from the reaction of calcium chloride with sodium bicarbonate in the rinse solution, cured the problem.

The catalytic action of iron in the oxidation of cellulose was known at least as early as 1920[E-8]. It is possible that the effect of iron in catalyzing (1) the oxidation of sulfur dioxide to sulfur trioxide and (2) the hydrolysis of cellulose, is much more important in the long-term stability of paper than was realized.

The degradation of the cellulose in cellulosic materials by light is influenced by three principal factors: sensitizers, oxygen and moisture[E-17a] (L. F. McBurney, chap. III.C.4). Cellulose is transparent to visible and near-ultraviolet light, but a sheet of paper appears practically opaque because of light scattering. As record materials contain many non-cellulosic materials, there is the possibility of direct photolysis, or of these materials acting as sensitizers. Many dyes and pigments act as photosensitizers by absorbing the light directly and transferring it to cellulose with degradation. The presence of oxygen is required for the photosensitized degradation of cellulose, and moisture appears to enhance degradation.

During the early 40's Launer made an extensive study of the effect of light on paper. Recognizing that much of the data in the literature was questionable due to inadequate temperature control, he devised and built an apparatus that maintained the temperature of the irradiated sheet within one or two degrees of the control temperature[A-33]. He was able to show that the temperatures of sheets that were not thermostated were so high that valid photochemical study was out of the question.

Although Launer used a carbon arc lamp, he used a filter that removed most of the infrared, and practically all of the energy below 320 nm. About 80% of the filtered arc light lay between ca. 330 and 440 nm. This is the part of the spectrum most likely to cause damage to paper in archives and libraries[A-43], as window glass cuts off everything below ca. 330 nm. The usual conditions of irradiation were 30°C and 58% R.H., although other conditions were used for certain purposes.

A summary of the principal findings of Launer's work is as follows:

(1) Papers that do not contain lignin normally are bleached by light in the absence of heat effects. This phenomenon had been reported earlier for specific experimental conditions[E-43].
(2) Photo-oxidation is the principal reaction(s) that occurs during the photodegradation of cellulose.
(3) A post-irradiation effect occurs in which papers are bleached during irradiation and then darken during storage in the dark. This effect has been noted by others[E-6], (p. 143).
(4) Photo-oxidation causes an increase in acidity, an increase in reducing power and a decrease in degree of polymerization.
(5) Lignin is extensively degraded during photo-oxidation. The analytical value for lignin in newsprint decreased from about 19% to about 14% during 17 h of irradiation.
(6) Lignin either acts as a sensitizer in newsprint, or its degradation products help degrade the cellulose in newsprint, or both.
(7) Newsprint is bleached by light in the absence of oxygen.
(8) Newsprint is greatly stablized against photo-oxidation by impregnation with sodium bicarbonate.
(9) Papers impregnated with acid were less stable toward light.





Although these data are empirical in nature and tell nothing definite about the actual mechanism of photodegradation, their usefulness for the archivist and librarian has never been surpassed.

Flynn studied the degradation of dried, purified cellulose in a vacuum with far-ultraviolet radiation (253.7 nm)[A-48,49,56,57]. Hydrogen, carbon monoxide, and carbon dioxide were evolved, aldehyde and carboxyl groups were produced in the cellulose, and the degree of polymerization decreased. The initial reactions were direct photolysis rather than the photo-oxidation that occurred in Launer's work, but a post-irradiation effect was still evident. Most of the aldehyde group formation took place during photolysis. Hydrogen, carbon monoxide and carbon dioxide evolutions increased with temperature. Chain scission and carboxyl group formation occurred to a large extent during the post-irradiative oxidation of long-lived oxygen-containing radicals. The dominant reaction appears to be the photolysis of alcohol groups.

### *2.7 Thermal Analysis*

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used at NBS as screening tests for developing information on the contributions of selected variables to the stability of papers. This approach proved to be very rewarding and several important variables were identified that later proved to be important to accelerated aging at 90°C and below[A-58,65,67,B-8,12].

DTA is a technique for studying the thermal behavior of materials as they undergo physical and chemical changes during heating. Differences in temperature between a sample and an inert material, as the two are heated at a constant rate, are plotted automatically on a chart. These temperature differ-

ences were used to fingerprint the relative thermal decompositions of various samples, as the temperatures at which various exotherms (evolution of energy) and endotherms (absorption of energy) occurred could be interpreted in relation to stability.

TGA is a technique for measuring the weight loss of a material during heating. TGA can give information on the relative thermal stability of cellulose modifications and on reactions that occur during heating.

As cellulose never emerges unscathed from the isolation and bleaching treatments it receives during processing, it will contain added aldehyde, ketone and carboxyl groups in various locations in the chain and in the anhydroglucose ring, depending on the type of isolation and type of bleaching. Aldehyde was found to contribute substantially to the thermal instability of cellulose. For carboxyl the trend was the same but not nearly as great as for aldehyde.

The most important contribution that the carboxyl group makes to stability is the final form in which it exists in paper. Carboxyls in cellulose almost always exist in the form of a salt, and the metal on the carboxyl contributes heavily to the stability (or instability) of paper. Stability is enhanced when the carboxyls are in the form of the calcium salt, but the aluminum salt form is unstable.

The mechanism of this effect is unclear. It may be nothing more than the greater acidity that exists in the aluminum modification. Also, the probability of one aluminum being attached to three carboxyls is vanishingly small. Some of the complexities of aluminum chemistry in relation to sizing have been discussed by others[E-44,45,46].

It is generally assumed that a major source of instability in paper is sulfuric acid generated from the reaction of water with papermarkers alum. If this is true, a sample of cellulose treated with alum should give a DTA plot similar to a sample of cellulose treated with sulfuric acid. These two plots are distinctly different, suggesting that acid produced from the reaction of alum and water is not the only factor in the degradation of paper by alum. These two plots also are different from a DTA plot of cellulose in which the carboxyls are covered by aluminum.

TGA plots of cellulose containing sulfuric acid showed that the residue remaining after the temperature had reached 500°C was much greater than without acid. This is an indication that crosslinking reactions had occurred during the heating.

DTA and TGA data were obtained on a group of 14 papermaking pulps with varying amounts of hemicellulose and of carboxyl contents. The calcium, aluminum and free acid modifications were prepared for evaluation. The data show that pH is a function of the carboxylic acid content, and that the DTA decomposition plots are related to pH. The calcium modifications were always





more stable than the aluminum modifications. There was some evidence that hemicelluloses have an important bearing on stability, but this was inconclusive. The carboxyl contents were closely related to the hemicellulose contents of the pulps.

DTA and TGA techniques show some promise of development into "quick" accelerated aging methods. It is questionable, however, whether these techniques ever would become standard methods, as the instrumentation is changing so rapidly that a method could be rendered obsolete while it was winding its way through the standards process. The apparatus used in this work, ca. 1970, is already out of date.

### *2.8 Preservation and Restoration*

In this area NBS has published on preservation of newspaper records, care of filmslides and motion picture films, lamination of documents, preservation of the United States Constitution and Declaration of Independence, and the preparation of material for cornerstones. In addition, a consumer booklet was published on conservation of records[A-66].

In 1934, Scribner published a report on preservation of newspaper records[A-18]. Prior to 1868 newspapers were printed on rag paper, but the introduction of ground wood pulp changed this, and most newspapers in storage beyond that date are in poor condition. In 1927 the New York Times initiated the practice of printing part of its daily edition on high grade paper for permanent files in libraries, and other newspapers adopted this practice. Apparently this practice was discontinued many years ago, probably with the coming of World War II, and the practice of microfilming newspapers for storage of information made this practice unnecessary.

"Reproduction in miniature appears to be the ideal means of preserving newspaper records". This quotation from Scribner referred to "... making miniature prints of newspaper records on transparent slides and projecting them in enlarged form for reading ...".

For preservation of newspapers not printed on special paper, the New York Public Library used japanese tissue pasted to both sides of each sheet with a mixture of rice starch and tapioca dextrin[E-47]. Unfortunately, the practice of deacidification was still a few years in the future.

Weber and Hill published guidelines in 1936 for the care of filmslides and motion picture films in libraries[C-2]. Data were presented on the moisture content of cellulose acetate and cellulose nitrate films as a function of relative humidity. It was shown that the folding endurance decreased as the moisture content decreased and that changes in moisture content caused dimensional

changes in filmslides and motion picture films. These changes usually were unimportant, but the curl resulting from uneven expansion of the film base and the gelatin layer could be troublesome. It is interesting that carbon tetrachloride was recommended as a cleaning fluid for filmslides, although its toxicity was recognized. It is unlikely that carbon tetrachloride, a carcinogen, would be recommended today.

The use of cellulose acetate film for protection of documents by lamination was first reported by Scribner in 1934 as a means of strengthening newspaper records[A-18]. It was determined only that the procedure was feasible. Scribner reported in 1940[A-34] an extensive evaluation of several cellulose acetate film and paper combinations, some of which were laminated by means of heat and pressure and some through the use of adhesives. The acetate films applied with heat and pressure were more stable toward accelerated aging than the ones applied using an adhesive. Extreme changes in relative humidity did not affect the laminations, and the process did not distort printing or writing. Although the work was well done for the time, the accelerated aging test was inadequate for cellulose acetate, and no work was done on the interactions of cellulose acetate and plasticizer with respect to stability, and to performance in lamination.

A project on preservation of documents by lamination was initiated in 1954 and NBS monograph No. 5 on this subject was issued in 1959[A-51]. The work was divided into the following tasks: (1) stability of cellulose acetate films, (2) plasticizer loss of cellulose acetate films, (3) degradation of film and paper during lamination, (4) tissue reinforcement, (5) deacidification, (6) special laminating methods, (7) preliminary study of films other than cellulose acetate, and (8) specifications for archival laminating film formulated from cellulose acetate. The principal objective was to develop the information necessary to write specifications for cellulose acetate film of commercially practicable quality that would have maximum stability and suitable physical properties.

An ideal laminating film could be described as having the following properties:

(1) It should be sufficiently flexible to withstand the flexing and folding required of a paper during use.
(2) It should be considerably stronger than the paper it protects.
(3) It should have the proper rheological properties. Within 2% elongation, the probable elongation of most papers, the film should show satisfactory strength at an elongation of much less than 2%.
(4) It should have considerable elongation beyond the yield point on a load-elongation curve, as this is associated with high edge tear.





(5) It should be resistant to abrasion.
(6) It should be stable over a long period of time, preferably centuries.
(7) Lamination should be a simple process, preferably without expensive equipment.
(8) It should be possible to remove the film, if this becomes necessary, easily and without damage to the paper.
(9) The film should be transparent to visible light.

There is no film on the market today that meets all of these requirements.

A cellulose acetate film without plasticizer cannot be laminated to paper. The proper kind and amount of plasticizer must be incorporated in the film in order to lower the softening point to the required temperature which is about 115°C.

The specific plasticizer is very important to stability: The ether-ester plasticizers cause a film to be very unstable, while triphenyl phosphate stabilizes a film. In addition, it is desirable to add to the formulation an acid acceptor, an antioxidant and an ultraviolet absorber. Such a film survived for about three months without appreciable degradation in moist oxygen at 124°C. Another experimental film with an ether-ester plasticizer was useless in four hours under the same conditions. The degradation was principally oxidative in nature. The degradation of cellulose acetate films is discussed more extensively in another publication[A-50].

A popular misconception about cellulose acetate laminating film is that plasticizer loss will cause the film to become brittle. An experimental film from which the plasticizer had been removed by a special procedure retained its flexibility. Films cast without plasticizer also were flexible. These films are one mil thick, and appreciably thicker films would give different results.

In order to check the degradation of cellulose acetate films in laminating presses, two commercial films were passed through 20 typical laminating cycles in three presses in the Washington area. There was no change in the viscosity of the film.

A rag paper with a pH of 4.9 was given the same treatment. Some yellowing occurred, and distinct lowering of viscosity was evident. The cylindrical presses, which operate at higher temperatures than the flatbed press, caused more pronounced changes. This was especially true for a sample of this paper that had been treated with alum solution before being run through the presses. These results indicate that paper normally should not be laminated without prior deacidification.

Tissue reinforcement improved most of the physical properties of two experimental papers, especially internal tear. Edge tear was somewhat different.

Edge tear was greatly improved when paper was laminated with film only, but the improvement was not spectacular when tissue was added to the lamination sandwich. It appears that tissue reinforcement could be omitted unless the document in question is in especially poor shape. This is a decision for the conservator.

The study of the effect of deacidification was not extensive, but it did show that deacidification nullified the effects of acid during accelerated aging. Data on the effect of washing and deacidification on the physical properties of two old all-rag papers showed that neither treatment damaged the papers.

Kathpalia[E-48] reported in 1958 on a solvent lamination technique that does not require a laminating press. A lamination sandwich of tissue, film, document, film, tissue is assembled on a flat surface, and acetone is applied with a non-linting cloth, starting at the center and wiping toward the edges. The sandwich is then turned over and the process repeated. The physical properties of this laminate compared favorably with those of laminates from a flatbed press.

A desk review of plastic films other than cellulose acetate that might be used for lamination did not turn up any serious contenders. At that time the concept of encapsulation had not surfaced.

Both composition and performance specifications for a cellulose acetate laminating film were prepared and included in NBS Monograph No. 5[A-51], but were not submitted to a standards organization. This probably should have been done. Only one film on the market could pass the specification requirements. This film no longer is a regular production item, but is made on special order when the accumulation of requests is sufficient to warrant the effort.

Although lamination is a valid conservation technique when preceded by deacidification, encapsulation probably will be used more and more where lamination formerly was used.

At the request of the Librarian of Congress, NBS prepared recommendations for the preservation and display of the Constitution of the United States and the Declaration of Independence, and these were submitted on March 16, 1940[A-40].

"It is recommended that both Documents be enclosed within sealed receptacles, and that the air within these receptacles be replaced with a chemically inert gas, such as nitrogen, helium, or argon, the gas to contain approximately 4 grains of moisture per cubic foot. By thus sealing the receptacles, the absolute humidity would be kept constant and low enough to avoid all possibility of excessively high relative humidities for the temperature range encountered. This would eliminate the danger of having excessive moisture in the Documents at any time. Storing the Documents in an inert gas will remove the





possibility of deterioration from oxidation, or from acid hydrolysis resulting from absorption of sulphur dioxide from the atmosphere".

These documents were made of animal parchment, which will last for centuries with proper care.

Helium was selected as the inert gas in the enclosures for the documents. In addition to not supporting organic life, it has a high thermal conductivity relative to air. For this reason, a thermal conductivity type of leak detector was built into the enclosures. These leak detectors are still functioning after more than 30 years.

As NBS had done considerable work on the effect of moisture on leather, it was a simple matter to suggest an amount of moisture that would provide a R.H. of 25 to 35% at room temperature. A high R.H. can allow the attack of micro-organisms even in the absence of air, and if the enclosures contain too much moisture, condensation can occur if the temperature drops for some reason.

The enclosures for the documents must be airtight, chemically inert, strong and transparent. For these reasons, the documents were enclosed between two sheets of tempered glass and the edges were sealed by soldering a lead strip to the glass, which had a special metallic coating to allow this operation. The enclosures were supplied by Libbey-Owens-Ford Glass Company, and their scientists performed the sealing operations. The enclosures were flushed for several days with humidified helium before the final sealing operation.

The documents were backed with sheets of paper made from cotton, and containing small amounts of calcium carbonate and titanium dioxide. The paper, made in the NBS paper mill, serves as a moisture reservoir to "damp out" any changes in relative humidity caused by temperature variations.

Damage from the lights used to illuminate the documents was prevented by a filter laminated between sheets of glass, and essentially no light below 480 nm reaches the documents.

After NBS and the Library of Congress brought this task to a successful conclusion, the documents were transferred to the National Archives on December 13, 1952. They are on display in a suitable shrine, and a motorized mechanism enables their transfer to a vault below the floor when the occasion warrants.

NBS has had many requests over the years concerning the storage of appropriate documents in cornerstones. Although definite guidelines have never been written down, the following are some suggestions that have been made to individuals who have asked for advice:

1. Contents of box
   (a) New paper records should be made on paper containing an alkaline filler.
   (b) Records already made on paper should be deacidified. Newspaper copies especially should be deacidified.
   (c) Permanent inks should be used for making records although, to our knowledge, no specifications exist for permanent inks.
   (d) Ordinary black and white photographs should have been thoroughly washed to remove residual hypo.
   (e) Manfacturers of magnetic tape should be consulted for recommendations concerning tape that should be used.
2. The cornerstone box
   (a) This should be a box within a box with space between the inner box and outer box of at least one inch, preferably two inches, of fiberglass insulation.
   (b) The boxes should be made of copper.
   (c) The boxes should have inlet and outlet tubes (copper) for flushing with helium or nitrogen gas.
   (d) The lid of the inner box should fit as tightly as possible, as it will not be welded shut.
3. Flushing and sealing the boxes
   (a) The inner box should be loaded with documents and flushed with dry helium or nitrogen for about one day.
   (b) The inlet and outlet tubes should be crimped shut at once, the box wrapped with fiberglass and placed in the outer box, the helium (or nitrogen) connected at once, and the outer box copper-welded shut.
   (c) The helium (or nitrogen) flushing should be continued for about an hour, and the tubes crimped and welded shut.

As there have been no controlled experiments in this area, one cannot guarantee results. This process will remove most of the air and most of the moisture from the boxes. This will prevent oxidative degradation, degradation due to moisture, and condensation of moisture on the records. Degradation of paper due to acid will be prevented by starting with stable paper.

### *2.9 Photographic Records*

NBS has been active in two photographic areas in research on conservation of records: stability of motion picture film in the 1930's, and a study of microfilm blemishes in the 1960's.





A confusing feature of the literature of the 1930's is that the term "microfilm" apparently had not surfaced. For example, the title of a publication by Hill and Weber in 1937[C-4] is entitled *Evaluation of Motion Picture Film for Permanent Records.* This is understandable, for the first use of photography for this purpose probably was with a motion picture camera, using motion picture film, with the operator hand-cranking the film one frame at a time.

The following quote from a paper by Scribner in 1939[C-7] leaves no doubt about the situation, and in addition, except for the terminology, it is a fairly accurate description of the world of microfilm today: "During the past decade, photographic films of the motion-picture type have assumed in the documentary field a position commensurate with that of paper. Of the many materials used for conveying information, such as stone, clay, metal, animal hide, and papyrus, paper first permitted the wide dissemination of knowledge at such low cost that printed matter ultimately became within the reach of everyone in the civilized countries and thus paper, together with printing, became a prime mover in the advance of civilization. But documentary material has now become so voluminous that it is neccessary to condense it; much is contained on impermanent paper and, therefore, must be preserved by reproduction in permanent form; it is desirable to render records which cannot be removed from depositories more accessible by reproducing them for distribution; and it is desirable to reproduce records to minimize wear of the originals by handling. The photographic films fulfill the requirements admirably because of the simplicity of the process of reproduction and its low cost, and the great reduction in the size of the record.

"Special cameras have been developed which automatically photograph on films successive images of pages of printed or written matter as fast as they can be passed before the lens. Various forms of reading devices have been devised, ranging from the small hand lens for direct reading to compact projectors which place the magnified image of the record before the reader in convenient form for reading at a desk, and which have means of turning film records in reel form to any desired image as readily as turning the pages of a book.

"In the conservation of storage space for records, the films are preeminent. At the U.S. Census Bureau, where all of the census records are being duplicated on film, the data on cards requiring 7,000 square feet of storage space are now contained on film requiring only 50 square feet. At the New York Public Library, one year's bound issue of the New York Times occupies a storage space of 108 cubic feet; duplicated on film the space is decreased to 1/3 cubic foot. The cost of reproduction is very low, particularly for large-scale operations. Many of the leading libraries, and other organizations, furnish film

copies of records on order at very small cost; as low as 1 cent or less per page for large orders.

"It is for these reasons that films have become a widely used record material. Nearly all of the larger organizations of the National Government make extensive use of them, the use of them as a part of library service has been mentioned, and they are used extensively for the records of department stores, banks, insurance companies, and many other commercial activities which require the keeping of extensive records. Several of the leading newspaper publishers are having issues that are printed on the usual impermanent paper filmed for storage".

We normally think of microphotography as an invention ca. 50 years old and, from a commercial point of view, this is not far wrong. The first microfilm camera for filming bank checks during the clearing process was installed in 1928, and a reader was supplied for reading microfilm copy. A system for microfilming newspapers was offered in 1934[E-49].

The first microphotograph on a daguerreotype plate – at 160x reduction – was made by Dancer in 1839, and in 1852 Dancer made the first collodion microfilms. Microfilm remained a novelty except for the "pigeon express" during the Franco-Prussian war of 1870–71, the microfilming of the records of an insurance company in 1871, and of the manuscripts of a Paris publisher in 1887[E-50].

In the 1930's NBS evaluated two types of films for use as permanent records. One was coated with a photographic emulsion, and the other had a light-sensitive dye incorporated in the base for forming the image. Cellulose acetate and cellulose nitrate were available at the time as bases for the emulsion type, and cellulose acetate and viscose sheet were available as bases for the dye type of photographic film[C-3,4,6,7]. The nitrate film, because of the fire hazard associated with its use and storage, was rejected as a permanent record material. In addition, it failed all of the tests that were devised to estimate probable stability.

It was concluded that cellulose acetate was the best film base, and that viscose base was acceptable for temporary records, but not permanent records. It was demonstrated (using the tools of the 1930's) that acetate films of both the emulsion type and the dye type were suitable for permanent records, if properly made for the purpose. Several tests were developed for evaluation of these films, including semimicro tests[C-5]. It was concluded that the hypo content of developed films should be very low to avoid yellowing at a later date.

The accelerated aging method that was developed for paper (72 h in a circulating oven af 100°C) also was used in estimating the relative stability of motion picture films. Other tests are under active development today.





For storage of film records, a R.H. of ca. 50%, a temperature range of 70°–80°F and removal of acidic gases and dust was recommended. A lower R.H. and a lower temperature range would be recommended today.

In the 1960's NBS conducted a research program on the nature and prevention of microscopic spots in processed microfilm. The first step was to make a survey of the microfilm stored in several U.S. Government repositories, and the results of this survey were reported in NBS Handbook 96[C-11]. Six types of aging blemishes were reported, and these apparently developed two to twenty years after the films were processed. This report describes these blemishes as well as the methods used to inspect, sample and report data.

Henn and Wiest have reported on the nature and prevention of spots in microfilm[E-51] and on the properties of gold-treated images[E-52]. The gold treatment was developed to prevent the formation of microscopic spots or aging blemishes that sometimes occur in stored processed microfilm.

Berg and Frei[E-53] have credited Reinders with being the first to study the redox-stability of the latent image[E-54]. Dichroic fog in film, which was ascribed to faulty processing, was reported as early as 1926[E-55].

A summary of the conclusions reached by McCamy and Pope[C-20] concerning steps to be taken to prevent the formation of microfilm blemishes are as follows:

(1) Use safety base permanent record film as specified by ANSI.
(2) Use no higher densities than are required for the intended purposes.
(3) Residual thiosulfate concentration should not exceed one microgram per square centimeter, but it should not be reduced to zero.
(4) Keep processing machinery and film clean.
(5) Avoid scratching the film.
(6) Store films in containers made of inert materials such as metals or some plastics.
(7) Storage temperature should not exceed 70°F and R.H. should not exceed 40%. (Henn and Wiest suggest that R.H. may be lowered to 20%, and that the temperature may be lowered to 55°F).
(8) Avoid wide-range cycling of temperature and humidity.
(9) Inspect films on a regular basis.
(10) Maintain records of processing and storage so that the next generation of archivists will be able to act on the basis of firm data.

One cannot say that the subject of microfilm blemishes is closed, but at least some guidelines for preventing the blemishes have been developed.

### *2.10 Magnetic Tape*

The research effort on magnetic tapes has been exploratory, and confined to qualitative wet chemistry involving a correlation of colorimetric changes with accelerated aging. While modern instrumental methods probably would be more sensitive, with or without chemical derivatization, the aging procedures still should be applicable[D-1].

Modern magnetic tapes usually consist of two discrete strata termed backing and binder, with the magnetic particles (iron oxide) dispersed in the binder. Typical backing materials, such as polyethylene terephthalate, are relatively inert; failure occurred during accelerated aging as a separation of backing and binder. As with any other organic macromolecule that degrades with time, the binder could be expected to degrade as a result of hydrolysis and oxidation (probably with synergesis). The measurable changes include depolymerization, crosslinking, and/or increases in concentration of functional groups – aldehydes, ketones, carboxylic acids, for example – and possible formation of shortlived peroxide intermediates. The net result is a change in physical properties of the composite tape, and at some point the tape will begin to lose information.

The situation with magnetic tapes is simply an example of the generalized problem with archival materials in estimating and measuring longevity. The first step is to devise accelerated aging procedures that effect degradation within a reasonable period of time. The second step is to develop information indicating the chemistry and rate of the degradation processes. The third step is to extrapolate the results, if possible, to the conditions under which the tape is likely to be stored. Aging atmospheres of moist air, dry air, moist nitrogen, and dry nitrogen (with moist defined, for example, as 50% R.H.) encompass an informative range of aging conditions. A temperature of 90°C is reasonably likely to provide rapid acceleration of normal "aging" processes.

Physical tests such as load elongation may be used to monitor the degradation of backing. The preliminary study indicated, however, that a combination of sensitive chemical and physical tests is required to predict probable failure. A highly sensitive technique for characterizing macromolecular species in dilute solution, including organometallic polymers[E-49-E-52] consists of size exclusion chromatography (SEC) coupled with selected detectors (element specific graphite furnace atomic absorption (GFAA) spectroscopy, functional group sensitive ultraviolet or infrared absorbance, mass sensitive differential refractive index, etc.). SEC-GFAA, coupled with one or more optical detectors, has the potential to fractionate binder materials, determine the molecular weight of the fractions, detect any changes in the association of iron or other metals with





macromolecular species, and correlate changes in functional group concentration (found in the preliminary study) with changes in the molecular properties. The versatility and simplicity of the technique suggests its application to the simultaneous detection of molecular and chemical changes necessary to characterize the accelerated aging of magnetic tapes.

After some parameter of accelerated aging has been identified, data on the change of this parameter with time of accelerated aging can be developed, and the point at which the tape begins to lose information or otherwise becomes useless, can be identified. Blank tapes can then be stored for monitoring, and the information on similar record tapes can be copied at the time when a physical or chemical change detected in the blank presages catastrophic deterioration.

The approach described above was started with a group of four samples of magnetic tape, of which the binders were proprietary secrets. All were partially soluble in hexane. Chromatographic methods were not available at the time, but changes in carboxyl content and peroxide content were noted. One of the tapes exhibited a definite oxygen absorption at 90°C. A few experiments with differential thermal analysis indicated differences in the mechanism of thermal decomposition between tapes obtained from different manufacturers, but no definite correlation with accelerated aging.

Although the preliminary report was very promising, it was not possible to pursue the project.

### *2.11 Development of Standards*

The key to utilization of results of scientific research on problems such as the conservation of records is the use of these data to the maximum extent possible for the development of standards through a standards organization. For a diversity of reasons, this has not been fully realized and properly implemented in the past, but considerable progress has been made.

One of the first of these standards was a test method for accelerated aging of paper for 72 h at 100°C. On the basis of work done in the Paper Section, test methods for the determination of alpha cellulose, copper number, pH and rosin were developed. All of these methods were adopted in principle by TAPPI, and revisions of these methods are still extant as TAPPI standards.

Some of the work on the stability of paper in the thirties ended up in specifications promulgated by the U.S. Congressional Joint Committee on Printing for paper for permanent records[E-60]. These specifications emphasize fiber content, "cellulose purity" (low alkali solubility and low reducing power) and a high pH (5.5, hot extraction), and are still in use today. Unfortunately, none of

this information was used to develop standards through a non-government standards organization.

On the basis of the work done at NBS, Congress assigned to NBS in 1940 the responsibility for maintenance of standards for reproduction of U.S. Government records prepared by photographic and microphotographic means. This task was assigned to the General Services Administration in 1957[C-12]. Much of the information developed at NBS found its way into ANSI standards.

As indicated in 2.8, both composition and performance specifications for cellulose acetate laminating film were prepared, but these were not submitted to a standards organization. If promulgated by a standards organization they would have had far greater dissemination, and would have been revised at regular intervals.

"Guidelines for the preservation of the Constitution and Declaration of Independence" is an example of a document that required the best scientific and technological talent available, but collaboration with a standards organization for its preparation was neither necessary nor desirable. Other states and countries may have similar problems (one such problem occurred recently), but each one should be approached with the best expertise available, using the U.S.A. experience, and any other, as a guide. Obviously, this sort of situation does not occur often.

One of the principal tasks in the development of specifications for permanent record papers (NARS program, 1966–78) was the generation of data necessary to write an accelerated aging method. As mentioned in 2.1, a draft of an accelerated aging procedure in air at 90°C and 25% R.H. has been approved by Working Group 12, Subcommittee 2, of ISO Technical Committee 6, and was accepted by SC 2 at a meeting in Atlanta in October, 1981. This procedure is based on the data obtained on accelerated aging at various R.H., and data from the comparison of accelerated aging with natural aging for 36 years[A-72,B-13,14,15]. This procedure has been written in TAPPI format and submitted to the proper committee for consideration.

A large body of data has been accumulated over the years showing that the stability of paper is at least an approximate function of the pH of the paper. Therefore, it was possible to write specifications for papers for permanent records based on pH. This was done as an interim measure (NARS program, 1960–78) until an accelerated aging procedure could be developed.

Four specifications for permanent record papers, based on pH, were developed and coordinated with ASTM. Three levels of permanence are described: maximum permanence, high permanence and medium permanence. For *maximum* permanence, an alkaline filler of calcium and/or magnesium carbonate is required. Such a paper is expected to last several hundred years. A





*high* permanence paper is defined as one that has a life expectancy in excess of 100 years, and has a pH in the range of 6.5–8.5. A *medium* permanence paper is expected to last at least 50 years and up to 100 years, and must have a minimum pH of 5.5, hot extraction method[E-21].

There are several reasons for including more than one level of permanence. In the first place, the maximum in stability is not always needed. As the maximum usually is more costly, it is not good economics to specify unneeded quality. Secondly, a paper with a minimum pH of 5.5 usually is an off-the-shelf item. As the availability of alkaline papers in the U.S. is somewhat limited, the choice may be one of getting a "degree" of permanence or having to settle for an unacceptable level of permanence. The situation is somewhat different in Europe where about 50% of writing and printing papers are manufactured with alkaline fillers, for the latter are readily available.

## 3. Present status of records material research at NBS

NBS is studying the stability of polyester film that is used as a substrate for magnetic film and for microfilm. The correlation between acid content and degradation of physical properties is being examined as well as the effect of air pollutants on stability.

NBS is also designing a statistical survey procedure that is meant to evaluate the condition of paper records at NARS. This is not an easy task, for quantitative data are almost impossible to develop, and appraisals must contain a high component of subjectivity.

Both of these projects are sponsored by NARS.

## 4. A look into the future standard

Predictions concerning the future of technology are not noted for their accuracy. In 1938 the president of a company that built steam locomotives said steam was here to stay. Nine years later a new president of the company announced that they no longer were making steam locomotives, (p. 501)[E-61]. Hertz did not think that the wireless waves he had discovered would have any practical application, (p. 549)[E-61]. Vannevar Bush (1945) was very impatient with people who believed in the potential feasibility of intercontinental missles, (p. 434)[E-61]. Although we cannot predict the future, a review of the past may

put some old and some new problems in perspective, and enable one to better plan for the future.

A review of the past tells us that more effort should have been made to direct research effort into standards developed through standards organizations. The work in the 1930's on the stability of paper is a prime example. Another example is the outstanding work of the Barrow Laboratory (Richmond, Virginia, no longer in existence) on the stability of polyvinyl acetate adhesives for bookbinding[E-62]. This was not written as a specification through a standards organization, so the information never has been implemented.

It appears to the authors that we should look to the future to devise experiments that will provide the data for an understanding of the solid-state reactions that occur during the aging of materials. This is basic in one way or another to practically every task in conservation of records. Science now has progressed to the point where we should be placing less effort on empirical approaches (e.g. Arrhenius plots), as useful as they have been, and more on trying to determine the significant chemistry underlying instability and stabilization.

One of the best sources of information and ideas concerning projects that should be pursued in conservation of records is the conservationists. They are concerned with the day-to-day problems and, over a period of years, have made observations on the basis of natural aging that are indeed valuable to the scientist.

## 5. Publications and reports on stability and conservation of records

This is not a list of references in the usual sense. The first four sections refer to NBS publications and reports and the fifth section includes references to non-NBS publications. The division is as follows:

A. NBS publications on stability and conservation of paper.
B. NBS technical reports on stability and conservation of paper submitted to NARS 1966–1980.
C. NBS publications and technical reports on photographic materials.
D. NBS technical report on magnetic tape.
E. Non-NBS publications pertinent to NBS records research.

A few technical reports are included in 5 A.

Only a fraction of the research supported by NARS 1966–78 has been published in the open literature, so a list of technical reports covering that period is





included in 5 B. Most of these reports are available from the National Technical Information Services (NTIS), Springfield, Virginia 22151, U.S.A.

The references in 5.A through 5.D are listed in chronological order. The references in 5.E are listed in order of their appearance in the text.

Most of these publications are out of print, but probably can be found in large technical libraries. As the information in earlier publications is summarized in this paper, and as research techniques and methods of evaluation have changed over the years, the need to consult earlier papers is minimal.

Not every publication relevant to records reseach at NBS has been referenced.

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## 6. SUMMARIES

### *Historical Survey of Research at the National Bureau of Standards on Materials for Archival Records*

Records at the National Bureau of Standards (NBS) show that interest in the stability of paper as a research area surfaced there about 1925. Work began about 1928 and this later was expanded to include photographic materials as well as polymeric materials of interest in the production or protection of records. Most of this research has been funded by government agencies (especially National Archives and Records Service (NARS)), by archival and library organizations and by industry, through trade organizations. With the exception of work in Sweden, which was of considerable help to NBS, little research on the stability of records was in progress elsewhere.

Research at NBS on stability of record materials has resulted in the following:

(1) Development of two procedures for the accelerated aging of paper.
(2) Proof that acidity in paper is the principal cause of degradation.
(3) Proof that a calcium carbonate filler contributes to the stability of paper.
(4) Information on condition of books in libraries.
(5) Specifications for paper for permanent records.
(6) Information on the effects of fumigants on paper.
(7) Information on the effect of sulfur dioxide on paper.
(8) A method for removal of sulphur dioxide from library air.
(9) Information on lamination of paper with cellulose acetate film.
(10) Information on stability of microfilm.
(11) Information on the effect of light on paper.
(12) Information on the nature and prevention of microspots in processed microfilm.
(13) Data showing that
  (a) Degradation appears to be a function of moisture content.
  (b) Degradation is affected by aluminum.
  (c) Degradation is partly oxidative.
  (d) Although there is a good correlation between natural aging and dry accelerated aging at 100°C, it appears that an accelerated aging procedure should have some moisture in the aging atmosphere.

NBS has made two comparisons of natural aging with dry accelerated aging. The first study was started in 1928 with a group of commercial papers, and the last tests were made 26 years later. As the samples did not cover a broad spectrum of variables recognized today to be important to stability, it was concluded only that there was a "fair" correlation between accelerated and natural aging. The second study was made with a group of papers made in 1936 in the NBS experimental paper mill and tested 36 years later. It was concluded that pH, alpha cellulose, copper number and





tearing strength after accelerated aging at 100°C for 72 h were reasonable indicators of stability. When those data are compared with data from accelerated aging of handsheets at 90°C, and 0% and 50% R.H., it appears that an accelerated aging atmosphere should contain some moisture.

A systematic study of the aging of handsheets at several temperatures and relative humidities indicated that degradation is a function of moisture content. It was found that the metal on the carboxyls was important to stability, and that aluminum was especially detrimental. As the wet strength increased during aging, it appears that crosslinking occurs. There is a pronounced decrease in moisture regain during moist aging, but only a slight decrease during dry aging. This decrease during moist aging is interpreted as an increase in crystallinity. From the extensive data generated on accelerated aging, it was concluded that aging at 90°C and 25% R.H. would best correlate with natural aging in a temperate zone. This procedure is in the process of becoming an ISO method.

Fifty years ago rag papers enjoyed a superior reputation for durability and permanence, and this opinion is retained to this day. NBS was able to show that papers made from highly purified wood pulp had excellent strength properties. It is now known that both rag and wood pulp papers cover a broad spectrum of stability and durability, and it becomes a matter of proper selection in the market place.

In the thirties NBS showed that inks made from ammonium ammoniumoxyferrigallate did not cause instability in paper. As fountain pens are almost obsolete, due to the widespread use of the ballpoint, this information is of little value today. A study of the permanence of writing made with ballpoint pens has not been made by NBS.

NBS improved many of the analytical methods for evaluation of cellulose and paper, such as pH, alkali solubility and reducing power.

NBS made many studies of environmental factors of importance to preservation, such as light, temperature, relative humidity and atmospheric contaminants. A study of the condition of books in libraries showed that the condition of the holdings was partly a function of air pollution. It was shown that an alkaline wash removed most of the sulfur dioxide from library air. A study of the effect of light, similar in spectral distribution to that passing through a window, showed that (1) papers usually are bleached during irradiation, (2) the principal reaction is photo-oxidation, and (3) a post irradiation effect occurs in which paper darkens during storage in the dark after irradiation.

Thermal analysis (differential thermal analysis (DTA) and thermogravimetric analysis (TGA)) was used successfully as a screening procedure for the relative stability of various cellulose modifications. The importance to stability of the metal salt form of the cellulose carboxyls was developed using thermal techniques. DTA might be useful as a quick accelerated aging method, but instrumentation is changing so rapidly that the probability of the development of a standard method is rather small.

The most important NBS work on preservation and restoration has been on lamination, deacidification, preservation of the United States Constitution and Declaration of Independence, and the development of guidelines for storage of records in cornerstones. In developing specifications for an archival laminating film of plasticized cellulose acetate, it was shown that the selection of plasticizers was crucial to stability, and that the film should contain an antioxidant, an ultraviolet absorber and an acid acceptor. Loss of plasticizer did not lead to embrittlement of the film. Deacidification enhances the stability of paper and, as comparatively high temperatures are reached in laminating presses, it is not advisable to laminate without deacidification.

Based on work done in the thirties, NBS concluded that microfilm was suitable for permanent records, and in the sixties recommendations were made, based on extensive laboratory work, for the prevention of formation of microspots in microfilm.

Although the work was not extensive enough to lead to standards, an approach to the estimation of stability of magnetic tape was developed.

With respect to standards, NBS developed the information for writing (1) the present U.S. Government standards for permanent record papers, (2) four ASTM standards for permanent record papers, (3) standards for a cellulose acetate laminating film and (4) several ANSI standards in the photographic area.

NBS presently is studying the stability of polyester film that is used in magnetic tape, designing a statistical survey procedure for evaluation of the condition of paper records in NARS, and developing information necessary to writing guidelines for storage of records. All of these projects are sponsored by NARS.

It is concluded that the work of research laboratories should be channeled as much as possible into the development of standards through a standards organization. Also, we need to examine possible techniques, or devise new ones, that will give us a better understanding of the solid-state reactions that occur during the aging of record materials.

## *Aperçu historique des recherches effectuees au National Bureau of Standards sur les materiaux des registres et des archives*

Les archives du National Bureau of Standards (NBS) montrent l'intérêt porté au domaine de recherche concernant la stabilité du papier qui remonte à l'année 1925 environ. Les travaux ont débuté aux environs de 1928 et ce domaine s'est étendu aux matériaux photographiques et aux polymères offrant un intérêt dans la production ou la protection d'archives. Une part importante de ces recherches a été financée par des organismes gouvernementaux (notamment National Archives and Record Services (NARS)) de même que par des organisations d'archives et de bibliothèques et par l'industrie par l'intermédiaire d'organisations commerciales. A l'exception de travaux effectués en Suède représentant un apport considérable pour le NBS, rares étaient les travaux de recherche effectués par ailleurs sur la stabilité des documents et des archives.

Les recherches du NBS sur la stabilité des matériaux d'archives ont conduit aux résultats suivants:

1) Mise au point de deux processus de vieillissement accéléré du papier.
2) Etablissement de l'effet de l'acidité du papier comme cause principale de dégradation.
3) Preuve de l'effet d'une charge de carbonate de calcium contribuant à la stabilité du papier.
4) Informations sur l'état des livres entreposés en bibliothèques.
5) Spécifications du papier servant à l'établissement de registres permanents.
6) Informations sur l'effet des fumigations sur le papier.
7) Informations sur l'effet de l'anhydride sulfureux sur le papier.
8) Méthode d'élimination de l'anhydride sulfureux de l'air des bibliothèques.
9) Informations sur le laminage du papier à l'aide d'un film d'acétate de cellulose.
10) Informations sur la stabilité des microfilms.
11) Informations sur l'effet de la lumière sur le papier.
12) Informations sur la nature et la protection contre les micro-tâches apparaissant sur les clichés de microfilms reproduits.
13) Données prouvant que
    a) La dégradation semble être fonction du taux d'humidité.
    b) La dégradation est influencée par l'aluminium.





    c) Les phénomènes de dégradation sont partiellement oxydatifs.
    d) Même si le degré de corrélation entre le vieillissement natural et le vieillissement accéléré à sec à 100°C est élévé, il semble qu'un processus accéléré de vieillissement devrait faire intervenir une certaine quantité d'eau dans l'atmosphère ambiante servant au vieillissement.

NBS a procédé aux comparaisons du vieillissement natural et du vieillissement accéléré à sec. Les premières études ont été entreprises en 1928 et portent sur une série de papiers de type commercial, les dernières mesures ayant été effectuées 26 ans après. Du fait que les échantillons ne couvraient pas une gamme importante de facteurs dont l'importance sur la stabilité est reconnue à l'heure actuelle, on conclut simplement que la corrélation entre le vieillissement accéléré et le vieillissement naturel était »valable«. Les deuxièmes études entreprises portèrent sur une série de papiers produits en 1936 à la papeterie expérimentale du NBS et testés à l'issue d'une période de 36 ans. Il a été conclu que le pH, la teneur en cellulose alfa, le taux de cuivre et la résistance à la déchirure après un vieillissement accéléré à 100°C pendant 72 heures représentaient des indicateurs raisonnables de stabilité. Lorsque ces données sont comparées aux résultats de vieillissement accéléré de feuillets soumis à une température de 90°C et à des humidités relatives de 0% et 50%, il semble que l'atmosphère servant au vieillissement accéléré devrait contenir une certaine humidité.

Une étude systématique du vieillissement des feuillets à des températures et des humidités relatives diverses a indiqué que la dégradation est fonction de la teneur en eau. Il est prouvé que la présence de minéraux sur les groupes carboxyliques joue un rôle important sur la stabilité et que l'aluminium exerce un effet spécialement préjudiciable. Du fait que la résistance á l'état humide s'accroît durant le vieillissement, des liaisons transversales s'établissent. Une perte notable du degré de réhydratation a lieu durant le vieillissement en phase humide alors que ce même paramètre est modéré durant le vieillissement à sec; la chute notée durant le vieillissement en environnement humide est interprétée comme une augmentation de la tendance à la formation de cristaux. Les données nombreuses acquises sur le vieillissement accéléré ont permis de conclure que le vieillissement à 90°C et à 25% d'humidité relative aurait le meilleur degré de corrélation avec le vieillissement naturel en zone tempérée. Cette procédure est sur le point d'être adoptée comme méthod ISO.

Il y a cinquante ans, les papiers de chiffons jouissaient d'une réputation de durabilité et de stabilité supérieure et cette opinion persiste de nos jours. NBS a pu démontrer que les papiers produits à base de pulpe de bois hautement purifiée présentaient des caractéristiques excellentes de résistance. A l'heure actuelle, nous savons que les papiers à base de chiffons et de pulpe de bois couvrent une gamme étendue de stabilité et de durabilité et que le problème consiste à procéder à une sélection adéquate sur le marché.

Durant les années 30, NBS a prouvé que les encres à base de gallate d'ammonium/ammonium-oxy-ferrique ne causent pas d'instabilité du papier. Du fait de la quasi-disparition des stylographes et de l'utilisation étendue des stylos à bille, cette information présente aujourd'hui une valeur réduite. Une étude portant sur la stabilité des écritures au stylo à bille n'a pas été effectué par le NBS.

NBS a amélioré de nombreuses méthodes analytiques d'évaluation de la cellulose et du papier, telles que le pH, la solubilité aux alcalins et le pouvoir réducteur.

NBS a procédé à de nombreuses études des facteurs de l'environnement présentant une importance pour la préservation, tels que la lumière, la température, l'humidité relative et les polluants atmosphériques. Une étude de l'état des livres dans les bibliothèques a prouvé que l'état des stocks dépendait en partie de la pollution atmosphérique. Il a été prouvé qu'un nettoyage alcalin permettait d'éliminer la quasi-totalité de l'anhydride sulfureux de l'air des bibliothèques. Une étude de

l'effet de la lumière, à répartition spectrale analogue à la lumière d'une fenêtre, a démontré que (1) les papiers sont normalement décolorés par l'irradiation, (2) la réaction principale est du type photo-oxydation, (3) un effet post-irradiatif s'exerce conduisant à un assombrissement du papier durant le stockage dans l'obscurité après irradiation.

L'analyse thermique (analyse thermodifférentielle (ATD) et analyse thermogravimétrique (ATG)) a permis de procéder à une classification valable de la stabilité relative des diverses modifications de la cellulose. L'importance de la stabilité des dérivés sous forme de sels minéraux des groupes carboxyliques de la cellulose a été révélée en utilisant des techniques thermiques. L'ATD peut s'avérer utile comme méthode de vieillissement accéléré, mais le domaine de l'instrumentation se développe si rapidement que la probabilité de mise au point d'une méthode standard est relativement faible.

Les travaux les plus importants du NBS sur la préservation et la restauration ont porté sur le laminage, la désacidification, la préservation/conservation des documents de la »Constitution et de la Déclaration d'Indépendance« des Etats-Unis et le développement de méthods indicatrices des types de stockage des documents dans des écoinçons. Lors de la mise au point de spécifications des films de laminage d'archives à base d'acétate de cellulose plastifié, il s'est avéré que la sélection des plastifiants était un élément crucial de stabilité et que le film devait contenir un anti-oxydant, un produit absorbant dans l'ultraviolet et un système récepteur d'acidité. La perte du film protecteur n'a pas conduit à un accroissement de fragilité du film. La désacidification accroît la stabilité, d'un papier et du fait que des températures assez élevées sont obtenues dans les presses de laminage, il n'est pas recommandé de procéder au laminage sans désacidification.

Sur la base de travaux effectués dans les années 30, NBS a conclu que le microfilm représente un élément adapté d'enregistrements permanents et, durant les années 60, des recommandations ont été faites basées sur des travaux de laboratoire importants tendant à prévenir la formation de microtâches sur les microfilms.

Bien que les travaux n'aient pas été suffisamment poussés pour pouvoir établir des normes, une méthode d'estimation préliminaire de la stabilité des bandes magnétiques a été mise au point.

Dans le domaine des normes, NBS a mis au point les informations nécessaires dans le domaine de l'écriture: (1) la norme actuelle du gouvernement des Etats-Unis concernant les papiers à effet d'enregistrement permanent, (2) quatre normes ASTM sur les papiers à effet d'enregistrement permanent, (3) normes s'appliquant à un film laminé d'acétate de cellulose et (4) diverses normes ANSI du domaine de la photographie.

A l'heure actuelle, NBS procède à l'étude de la stabilité du film polyester utilisé dans les bandes magnétiques et met au point une procédure d'étude statistique permettant l'évaluation de létat des documents à base de papier au NARS. Le NBS met aussi au point les informations nécessaires afin de rédiger les indications principales à suivre lors du stockage de documents. L'ensemble de ces projects est financé par le NARS.

En conclusion, les travaux des laboratoires de recherche devraient être orientés autant que possible vers la mise au point de normes par l'intermédiaire d'une organisation traitant des normes. La nécessité d'examiner des techniques potentielles ou de concevoir des techniques nouvelles nous confère une meilleure compréhension des réaction à l'état solide se déroulant durant le vieillissement des matériaux d'enregistrement.





## *Historischer überblik über die Forschungstätigkeit des »National Bureau of Standards« in verbindung mit stoffen für Archivaufzeichnungen*

Akten des »National Bureau of Standards« (NBS) zeigen, dass das Interesse an der Stabilität von Papier als Forschungsgebiet hier etwa im Jahre 1925 auftauchte. Die Arbeit begann etwa 1928 und umfasste später auch fotografische und polymere Materialien, die bei der Herstellung oder für den Schutz von Aufzeichnungen von Interesse sind. Der grösste Teil der hiermit verbundenen Forschungsarbeiten wurde von staatlichen Behörden getragen (vor allem soll hier der »National Archives and Records Service« (NARS genannt sein). Des weiteren wurde die Arbeit von Archiv- und Bibliotheksorganisationen sowie der Industrie gestützt. Mit der Ausnahme von Schweden, wo die Forschungstätigkeit auf diesem Gebiet eine bedeutende Unterstützung für NBS darstellte, wurde in anderen Ländern der Erforschung der Stabilität von Aufzeichnungen kaum Bedeutung beigemessen.

Die Forschung des NBS auf dem Gebiet der Stabilität von Archivmaterialien hat zu folgenden Ergebnissen geführt:

1) Entwicklung von zwei Verfahren zur beschleunigten Alterung von Papier.
2) Beweiserbringung, dass die Säure in Papier die Hauptursache für den Qualitätsabbau ist.
3) Beweiserbringung, dass ein Kalziumkarbonat-Füllstoff zur Stabilität von Papier beiträgt.
4) Informationen über den Zustand von Büchern in Bibliotheken.
5) Papierspezifikationen für bleibende Aufzeichnungen.
6) Informationen über die Einflüsse von Desinfektionsmitteln auf Papier.
7) Information über die Einflüsse von Schwefeldioxid auf Papier.
8) Entwicklung einer Methode zur Beseitigung von Schwefeldioxid aus der Luft in Bibliotheken.
9) Informationen über die Beschichtung von Papier mit einer Zelluloseazetat-Schicht.
10) Informationen über die Stabilität von Mikrofilmen.
11) Informationen über die Auswirkungen von Licht auf Papier.
12) Informationen über die Beschaffenheit und Verhütung von Mikroflecken in entwickelten Mikrofilmen.
13) Daten, die beweisen, dass
    a) Qualitätsabbau eine Folge von Feuchtigkeitsgehalt ist,
    b) Qualitätsabbau von Aluminium beeinflusst wird,
    c) Qualitätsabbau teilweise oxidativ ist.
    d) Obgleich zwischen natürlicher und trockener beschleunigter Alterung bie 100°C eine gute Korrelation besteht, erscheint das Vorhandensein von etwas Feuchtigkeit in der Alterungsatmosphäre angebracht.

NBS hat zwischen natürlicher und trockener beschleunigter Alterung zwei Vergleiche durchgeführt. Die erste Untersuchung wurde im Jahre 1928 mit einer Reihe handelsüblicher Papiere begonnen, die letzten Tests 26 Jahre später abgeschlossen. Da die Muster nicht das breite Spektrum an Variablen umfassten, die heute für die Stabilität als wesentlich bekannt sind, wurde lediglich die Schlussfolgerung gezogen, dass zwischen beschleunigter und natürlicher Alterung »eine Beziehung« besteht. Die zweite Untersuchung umfasste eine Reihe von Papierqualitäten, die 1936 in der Versuchs-Papierfabrik des NBS hergestellt und 36 Jahre später getestet wurden. Aus diesen Tests wurde die Schlussfolgerung gezogen, dass pH, Alfazellulose, Kupferzahl und Zerreissfestigkeit nach beschleunigter Alterung unter den Bedingungen 100°C und 72 Stunden akzeptable Indikatoren für die Stabilität sind. Werden diese Daten mit Daten vergleichen, die sich aus der beschleunigten Alterung von Bögen bei 90°C sowie 0% und 50% relativer Feuchtigkeit erge-

ben, so kan daraus gefolgert werden, dass eine beschleunigte Alterungsatmosphäre etwas Feuchtigkeit enthlaten sollte.

Eine systematische Untersuchung der Alterung von Papierbögen bei verschiedenen Temperaturen und relativer Feuchtigkeit zeigte, dass der Qualitätsabbau eine Folge des Feuchtigkeitsgehaltes ist. Es wurde festgestellt, dass das Metall der Carboxyle ausschlaggebend für die Stabilität ist, wobei sich Aluminium als besonders schädlich erwies. Da die Nassfestigkeit während der Alterung zunahm, kann hieraus die Bildung von Querverbindungen gefolgert werden. Bei feuchter Alterung ist eine ausgeprägte Reduzierung der Feuchtigkeitswiedergewinnung zu konstatieren, während bei der trockenen Alterung nur eine geringe Reduzierung festgestellt werden kann. Die bei der feuchten Alterung festgestellte Reduzierung wird durch die steigende Kristallisierung erklärt. Aus dem umfangreichen Datenmaterial, das aus der beschleunigten Alterung gewonnen wurde, ist die Schlussfolgerung gezongen worden, dass eine Alterung bei 90°C und 25% relativer Feuchtigkeit am besten der natürlichen Alterung in einer gemässigten Zone entsprechen. Dieses Verfahren ist im Begriff, sich als ISO-Methode zu entwickeln.

Vor 50 Jahren genoss Hadernpapier wegen seiner Haltbarkeit und Beständigkeit das höchste Ansehen; diese Ansicht besteht auch heute noch. NBS konnte beweisen, dass Papier, das aus völlig gereinigter Holzmasse hergestellt wird, über eine ausgezeichnete Festigkeit verfügt. Es is t jetzt bekannt, dass sowohl Hadern- als auch Holzmassepapier über eine gute Stabilität und Haltbarkeit verfügen. Die jeweils vorzuziehenden Eigenschaften sind vom Verbraucher genau zu wählen.

In den dreissiger Jahren bewies NBS, dass Tinte aus Ammonium Ammoniumoxyferrigallat die Stabilität von Papier nicht negativ beeinflusst. Da Füllfederhalter jedoch kaum noch verwendet werden, ist diese Tatsache heute von wenig Wert. NBS hat die Stabilität der Kugelschreiberschrift nicht untersucht.

NBS har viele der analytischen Methoden zur Bewertung von Zellulose und Papier verbessert, davon sollen pH, Alkali-Löslichkeit und Reduzierfähigkeit genannt werden.

NBS hat viele Untersuchungen über Umgebungsfaktoren angestellt, die für den Schutz von Bedeutung sind, so z.B. licht, Temperatur, relative Feuchtigkeit und atmosphärische Verunreinigung. Eine Untersuchung des Zustandes der Bücher in Bibliotheken zeigte, dass der Zustand der Bestände auch von der Luftverunreinigung abhängig war. Es wurde bewiesen, dass ein alkalische Wäsche den grössten Teil des Schwefeldioxids aus der Bibliotheksluft entfernen konnte. Eine Untersuchung der Einwirkung von Licht, das in der spektralen Verteilung dem ähnlich ist, das durch das Fenster eintritt, zeigte (1), dass Papier in der Regel während der Bestrahlung verbleicht, (2) die hauptsächliche Reaktion ist Photo-Oxidation, danach (3) tritt ein Nachbestrahlungseffekt ein, d.h. Papier wird dunkler, wenn es nach der Belichtung im Dunklen gelagert wird.

Thermische Analysen (thermische Differentialanalyse (DTA) und thermogravimetrische Analyse (TGA)) haben sich als Screening-verfahren für die relative Feuchtigkeit von verschiedenen Zellulosearten als zweckmässig erwiesen. Mit Hilfe von thermischen Verfahren wurde die Wichtigkeit der Stabilität der Metallsalzform von Zellulose-Karboxylen entwickelt. DTA kann als schnell beschleunigte Alterungsmethode nützlich sein, die Messmethoden entwickeln sich jedoch so schnell, dass die Wahrscheinlichkeit sehr gering ist, dass hier eine Standardmethode entwickelt werden kann.

Die bedeutendste Erhaltungs- und Restaurierungsarbeit des NBS war die Laminierung, Entsäuerung und Konservierung der Verfassung und der Unabhängigkeitserklärung sowie die Entwicklung von Richtlinien für die Lagerung von Aufzeichungen in Ecksteinen. Bei der Entwicklung der Spezifikationen für eine dauerhaltbare Laminatschicht-Herstellung aus plastiziertem Zelluloseazetat wurde gezeigt, dass die Auswahl des Weichmachers einen entscheidenden Einfluss auf die Stabilität hat und dass die Schicht einen Antioxidanten, einen ultravioletten Absorber sowie einen Säureakzeptor enthalten sollte. Verlust an Weichmacher verursachte nicht eine sprödere Schicht.





Eine Entsäuerung verbessert die Stabilität von Papier und da in Laminatherstellungspressen relativ hohe Temperaturen erreicht werden, ist eine Laminatherstellung ohne Entsäuerung nicht ratsam.

Auf der Grundlage von Untersuchungen, die in den dressiger Jahren ausgeführt worden waren, kam das NBS zu der Schlussfolgerung, dass Mikrofilme für dauerhafte Aufzeichnungen geeignet sind. In den sechziger Jahren wurden diese Untersuchungen durch Empfehlungen ergänzt, wie die Mikroflecken in Mikrofilmen vermieden werden können. Diese Empfehlungen beruhen auf umfangreichen Laboratorienversuchen.

Man näherte sich auch der Einschätzung der Stabilität von Magnetischen Bändern, obgleich diese Arbeiten nicht umfassend genug waren, um zu normen zu führen.

Was die Normen betrifft, so hat NBS die Information zum Schreiben (1) der Normen der jetzigen Regierung der USA für dauerhafte Aufzeichnungspapiere entwickelt, (2) vier ASTM-Normen für dauerhafte Aufzeichnungspapiere, (3) Normen für eine Laminatschichtherstellung aus Zelluloseazetat und (4) verschiedene ANSI-Normen auf dem fotografischen Gebiet.

NBS untersucht zur Zeit die Stabilität der Polyesterschicht, die in Magnetbändern verwendet wird, erarbeitet ein statistisches Prüfungsverfahren zur Einschätzung des Zustandes, in dem sich Papieraufzeichungen im NARS befinden, und entwickelt die notwendigen Richtlinien für die korrekte Aufbewahrung von Aufzeichnungen. Die genannten Projekte werden vom NARS getragen.

Man kommt zu der Schlussfolgerung, dass die Arbeit von Forschungslaboratorien so weit wie möglich durch eine Normorganisation in die Richtung gelenkt werden soll, wo Normen entwickelt werden. Darüber hinaus müssen wir mögliche technische Verfahren untersuchen oder neue erfinden, die uns ein besseres Verständnis über die Vorgänge im Zusammenhang mit der Alterung von Aufzeichnungsmaterialien vermitteln.

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# Nuclear Magnetic Resonance Study of Parchment and Leather

*by* YU. P. PETUSHKOVA & G. M. NIKOLAEV

A knowledge of the condition and water content in parchment and book-binding leather of different origins is important for solving the problems of preserving medieval parchment and leather book-bindings. Water content in these materials depends not only on ambient humidity and temperature, but also on the structure of their protein macromolecules, primarily the collagen fibres, which constitute the base of the material. Nuclear magnetic resonance and calorimetric investigations have demonstrated that the hydration shell of the triplicate helix of collagen is heterogeneous and includes three water fractions, i.e. "free", "bound", and "rigidly bound[1]". Investigations of water hydrated by protein macromolecules could provide a clue to understanding the properties of surface protein structures.

In the work reported here, we used the nuclear magnetic resonance (NMR) technique for measurements of relaxation charateristics of the outer hydration layer in samples of medieval and modern book binding parchment, as well as in leather book-covers and wool, the latter being used for comparison for the keratin it contains.

## Materials and Methods

Fragments of several parchments, book-binding leather and wool, 0.5 g each, were freeze-dried under vacuum ($10^{-3}$ Hg mm) for 10–15 h, then placed in a desiccator and kept at a given relative humidity and a temperature of 4°C for 7 days. Saturated salt solutions with excess solid phase[2] were used to obtain desired R.H. Water proton relaxation characteristics of samples with different degrees of moistening were measured on a modified NMR spectrometer provided with digital readout and data storage facilities[3]. Proton resonance was observed at 17 MHz. Measurements of proton spin-spin relaxation times ($T_2$) were carried out by the Hahn two-pulse method[4]. Estimation of $T_2$ values from the spin-echo decay curves was done by a method described in Aksenov & Nikolaev[5]. Freeze-drying was used for the estimation of water content by an "equilibrating weighing" method.

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## Results

Relaxation characteristics of water protons are a direct reflexion of their mobility in a sample. They are different for water fractions having different degrees of binding to protein macromolecules. For free water, the proton spin-spin relaxation time, $T_2$, is 2–3 s. For protons of frozen free water, $T_2$ is about $10^{-6}$s. Values intermediate between these two correspond to water fractions with different degrees of motion and different degrees of interaction with the polar groups of the proteins. Strongly bound ("hydration layer") water is an integral part of collagen structure and has an ice-like rigid lattice configuration[6]. This water, for which $T_2$ is about $10^{-5}$–$10^{-6}$s, is outside the measurement range of our equipment, which can register times as short as $10^{-4}$ s minimum. The amplitude of the spin-echo signal is a direct measure of the number of protons contributing to the resonance. Using the spin-echo amplitude value, the water content in a sample can easily be calculated.

In the work reported here, we measured relaxation characteristics of the hydration water layers of medieval (XIV century), modern (XX century) and book-binding (XVII century) parchments, a XIX-century leather book-binding fragment and a wool (XIX century) sample, moistened to a varied extent by equilibrating the sample with the desired relative humidities.

Placing the samples under high humidity conditions (86%, 95%, 98%,

Table 1. Water content (%) in parchment, leather and wool samples equilibrated with different ambient relative humidities as determined by NMR (1) and "equlibrating weighing" (2) methods.
Table 1. Teneurs en eau (%) du parchemin, d'échantillons de cuir et de laine mis en équilibre à différentes humidités relatives ambiantes: détermination par méthode RMN (1) et par méthodes de «pesées à l'équilibre» (2).
Tabelle 1. Wassergehalt (%) in Pergament-, Leder- und Wollstücken, die bei unterschiedlicher relativer Umgebungsfeuchtigkeit im Gleichgewicht gehalten werden, wie dieser durch NMR- (1) und »Ausgleichs-Wiege-« (2) Methoden bestimmt worden ist.

| R.H. (%) | New modern parchment | | Medieval parchment | | Book-binding parchment | | Book-binding leather | | Wool tissue | |
|---|---|---|---|---|---|---|---|---|---|---|
| 55 | 11±0.8 | 14±1.0 | 11±0.8 | 16±1.1 | 5±0.4 | 11±0.8 | 4±0.3 | 7±0.5 | 11±0.8 | 9±0.6 |
| 65 | 13±0.9 | 19±1.3 | 12±0.8 | 21±1.5 | 9±0.6 | 18±1.3 | 7±0.5 | 13±0.9 | 6±0.4 | 11±0.8 |
| 75 | 15±1.1 | 21±1.5 | 14±1.0 | 24±1.7 | 11±0.8 | 20±1.4 | 8±0.6 | 14±1.0 | 8±0.6 | 12±0.8 |
| 86 | 18±1.3 | 23±1.6 | 19±1.3 | 25±1.8 | 16±1.1 | 20±1.4 | 11±0.8 | 13±0.9 | 12±0.8 | 13 |
| 95 | 20±1.4 | 26±1.8 | 21±1.5 | 28±2.0 | 19±1.3 | 24±1.7 | 11±0.8 | 14±1.0 | 9±0.6 | 14±1.0 |
| 98 | 18±1.3 | 26±1.8 | 18±1.3 | 29±2.1 | 16±1.1 | 23±1.6 | 11±0.8 | 16±1.1 | 9±0.6 | 14±1.0 |

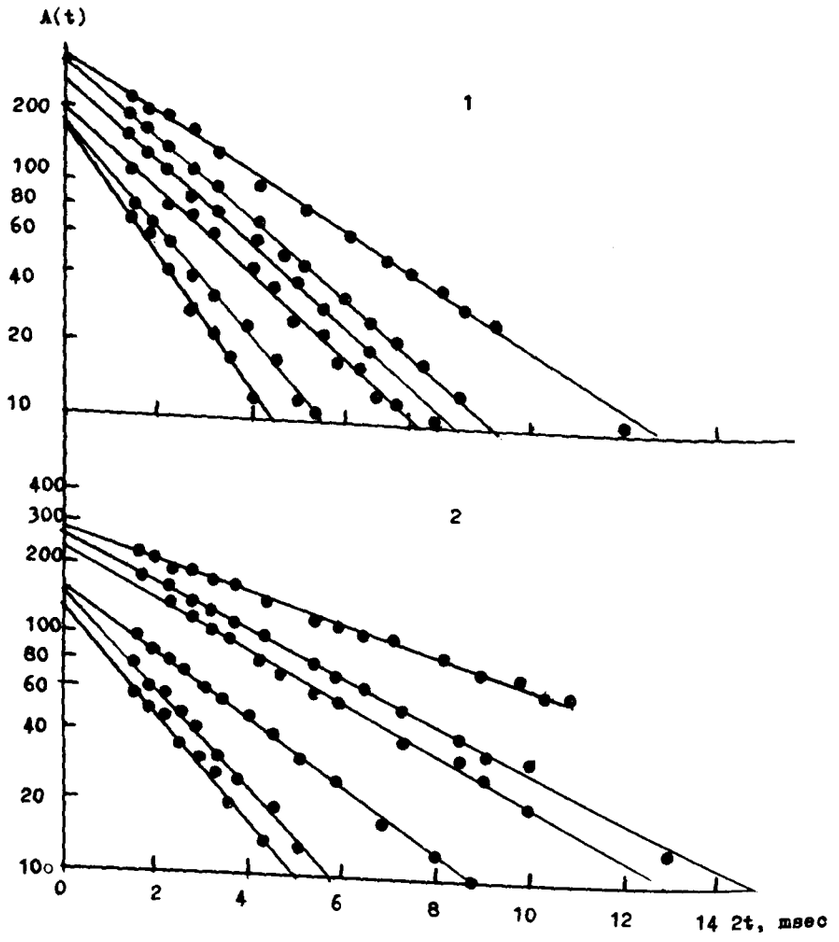


Fig. 1. Water proton transverse magnetization delay in modern (1) and ancient (2) parchments equilibrated with different relative humidities. A(t) – spin-echo amplitude, t – time spacing between 90° and 180° pulses. A dry weight: modern parchment – 0.3908 g, medieval parchment – 0.2952 g.

Fig. 1. Retard de magnétisation transversale du proton de l'eau dans des parchemins modernes (1) et anciens (2) mis en équilibre à différentes humidités relatives A(t) – amplitude de l'écho de spin, t – intervalle entre les pulsations à 90° et à 180°. A poids sec: parchemin moderne – 0,3908 g, parchemin moyennageux – 0,2952 g.

Abb. 1. Verzögerung der Transversalmagnetisierung von Wasserprotonen in mordernem (1) und altem (2) Pergament, das bei unterschiedlicher relativer Feuchtigkeit im Gleichgewicht gehalten wird. A(t): Spin-Echo-Amplitude, t: Zeitintervall zwischen 90°- und 180°-Impulsen. Trockengewicht: modernes Pergament – 0,3908 g, Pergament aus dem Mittelalter – 0,2952 g.



Table 2. Spin-spin relaxation time $T_2$ (ms) of water protons in parchment, wool and leather samples equilibrated with different relative humidities.
Table 2. Temps de relaxation spin-spin $T_2$ (ms) des protons de l'eau dans des échantillons de parchemin, de laine et de cuir mis en équilibre à différentes humidités relatives.
Tabelle 2. Spin-spin-Abklingzeit $T_2$(ms) der Wasserprotonen in Pergament-, Wolle-, und Lederstücken, die bei unterschiedlicher relativer Feuchtigkeit im Gleichgewicht gehalten werden.

| R.H. (%) | New modern parchment | Medieval parchment | Book-binding parchment | Book-binding leather | Wool tissue |
|---|---|---|---|---|---|
| 55 | 0.18±0.02 | 0.21±0.02 | 0.20±0.02 | 0.19±0.02 | 0.16±0.02 |
| 65 | 0.19±0.02 | 0.24±0.02 | 0.22±0.02 | 0.24±0.02 | 0.20±0.02 |
| 75 | 0.25±0.03 | 0.33±0.03 | 0.33±0.03 | 0.28±0.03 | 0.22±0.02 |
| 86 | 0.26±0.03 | 0.38±0.04 | 0.32±0.03 | 0.29±0.03 | 0.25±0.03 |
| 95 | 0.27±0.03 | 0.45±0.05 | 0.37±0.04 | 0.32±0.03 | 0.27±0.03 |
| 98 | 0.33±0.03 | 0.53±0.05 | 0.58±0.06 | 0.42±0.04 | 0.32±0.03 |
| 100 | 0.38±0.04 | 0.73±0.07 | 0.76±0.08 | 0.52±0.05 | 0.38±0.04 |

100%) gives rise to the spin-echo signal, which means an increase in water content (Table 1). Comparison of the water content estimations made by the NMR and "equilibrating weighing" methods shows that the NMR measurements give somewhat smaller values. This is because the equilibrating weighing method includes both the bound and "hydration" water fractions, whereas the latter escapes detection in NMR measurements because of resticted measurement range of the equipment used. Both methods show, however, that in collagen-containing materials the water content increases by an order of 2–4, as the R.H. is increased from 55% to 100%. Compared with these, the moistening of wool, which contains keratin, occurs to a much lesser extent under such humidity conditions.Note that the proton spin-echo relaxation decays observed in our experiments are exponential in character and are, hence, a single component. As an example, Fig. 1 represents a semi-logarithmic plot of spin-echo decay curves for a medieval and modern parchment. A similar single component behavior pattern was observed in all of the samples under investigation.

At humidities of 55% and 65%, in all the samples the spin-spin relaxation time of protons responsible for resonance was found to be about 0.2 ms (Table 2), a value characteristic of bound water with restricted motions. With the ambient humidity increased to 98% and 100%, the samples show significant differences in $T_2$. The modern parchment, leather and wool samples exhibit $T_2$ of about 0.4 ms, whereas the medieval (XIV century) and book-binding (XVII century) parchments have $T_2$ two times higher (0.7–0.8 ms). Thus, in modern

Table 3. Effects of "distant" moistening treatment on relaxation characteristics of water protons in XVI$^{th}$ century chart.
Table 3. Effets du traitement d'humidification (type à «distension») sur les caractéristiques de relaxations des protons de l'eau d'une carte du XVIème siècle.
Tabelle 3. Auswirkungen der Behandlung durch »Fern« befeuchtung auf die Abklingeigenschaften von Wasserprotonen in einer Karte aus dem XVI. Jahrhundert.

| Sample | Spin-spin relaxation time (ms) | Water content (%) |
|---|---|---|
| Control (without treatment) | 0.13 | 15 |
| After treatment by "distant" moistening method | 0.14 | 22 |

and medieval parchments, the protons of water bound to collagen exhibit different relaxation behavior only at high R.H. (98% and 100%). The most probable explanation for this is that phase transitions in the collagen lattice occur only with relatively high moistening[7]. Since the water adsorbate and the protein matrix constitute a single heterogeneous molecular phase, changes in collagen structure cause a change in the state of the bound water fraction. It is probable that the appearance of water with relatively high mobility that has been observed in the medieval parchment is brought about by changes in the surface layer of the parchment, caused by prolonged storage.

We also carried out NMR probing of a fragment of a XVI century chart, which was aimed at restoration. Treatment of deformed parchments is accomplished by the method of distant (gradual) moistening. It was of interest, in this regard, to examine the extent of parchment moistening and the state of water in it after it had been straightened out. A fragment of the same parchment, without performing straightening, served as a control. Following distant moistening treatment, the sample was placed under a press for 10 days to dry. NMR measurements were done under dry air conditions (R.H. 65%, 20°C). As is seen in Table 3, the parchment does not show, after treatment, any appreciable change in $T_2$, which is close to $T_2$ of water with little mobility. The water content appears to increase in a straightened chart sheet, compared with the control. It is thought that after moistening, the adsorbed water binds to the protein matrix, and for this reason it is not removed by subsequent drying under a press. The increase in water content with restricted mobility explains the fact that after distant moistening treatment the parchment resumes its softness and elasticity.





## Summaries


### *Nuclear Magnetic Resonance Study of Parchments and Leather*

The NMR technique was used for probing relaxation characteristics of water in the outer surface layer in samples of medieval and modern parchment, book-binding parchment, leather, and in a fragment of a wool tissue, which were equilibrated with different R.H. – 55%, 65% 75%, 86%, 95%, 98%, 100%.

On moistening the sample (with R.H. of the ambient varied from 55% to 100%), the amplitude of the NMR spin-echo signal increases to a greater extent in collagen-containing samples (parchments, leather), compared with wool, which contains keratin.

Modern and medieval parchments show different spin-spin relaxation times under high humidity conditions (98% and 100%). After straightening out the ancient parchment by the method of 'distant' moistening, the water content in the parchment is increased, with the relaxation time remaining without change.

### *Etude de resonance magnetique nucleaire de parchemins et de cuir*

La technique RMN a été utilisée pour démontrer les caractéristiques de relaxation de l'eau de la couche superficielle externe d'échantillons de parchemins moyennageux et modernes, de parchemin et de cuir utilisé en reliure de livres et d'un fragment de tissu laineux qui ont été mis en équilibre à différentes humidités relatives – 55%, 65%, 75%, 86%, 95%, 98%, 100%.

Lors de l'humidification de l'échantillon (à une humidité relative ambiante variant de 55 à 100%) l'amplitude du signal de l'écho-spin RMN augmente dans des proportions accrues dans les échantillons contenant du collagène (parchemin, cuir) comparé à la laine qui contient de la kératine.

Les parchemins modernes et moyennageux donnent des durées de relaxation spin-spin différentes dans des conditions d'hygrométrie élevée (98 à 100%). Après redressement du parchemin ancien par la méthode d'humidification avec distension, la teneur en eau du parchemin est accrue sans modification de la durée de relaxation.

### *Nuklearmagnetische Resonanz-Studie von Pergament und Leder*

Die NMR-Technik diente der Untersuchung der Abklingeigenschaften von Wasser in der Oberflächen-Schicht von Pergamentstücken aus dem Mittelalter und der Gegenwart, von Buchbinderpergament und Leder sowie einem Stück Wollgewebe. Die genannten Stücken wurden bei unterschiedlicher relativer Feuchtigkeit im Gleichgewicht gehalten – 55%, 65%, 75%, 86%, 95%, 98% und 100%.

Sofort nach dem Befeuchten eines Stücks (bei einer relativen Feuchtigkeit der Umgebung von 55% bis 100%), steigt die Amplitude des NMR-Spin-Echo-Signals mehr in kollagenhaltigen Stücken (Pergament, Leder) als in Wolle, die Keratin enthält.

Modernes und mittelalterliches Pergament weisen bei einem hohen Feuchtigkeitsgehalt unterschiedliche Spin-Spin-Abklingzeiten auf. (98% und 100%). Nach dem Glätten des alten Pergaments mittels der »Fern« Befeuchtung steigt der Wassergehalt im Pergament, die Abklingzeit bleibt unverändert.

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# Index



*Complete Table of Contents of this Symposium is found on pp. 3–4.