

Restaurator

1980 - VOL. 4. NO. 3-4



A

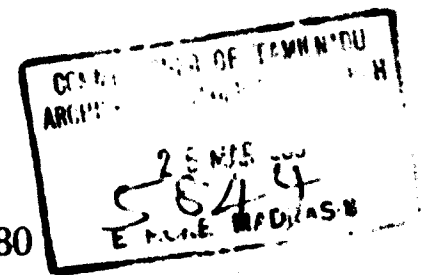
2: 885ml, N80.

N80.4.3

49970

International Journal for the Preservation
of Library and Archival Material

Volume 4 • Number 3-4 • 1980



MUNKSGAARD · COPENHAGEN

85 ml, 1980
1980-4-3
2972

Board of Editors

EDITOR:

POUL A. CHRISTIANSEN, Librarian. University Library: Scientific and Medical Dept. DK-2200 Copenhagen N, Denmark.

ASSOCIATE EDITORS:

N. S. BAER, Professor. New York University, Institute of Fine Arts: Conservation Center. 1 East 78th Street, New York, NY 10021, U.S.A.

GÜNTER BRANNHILF, Conservator. University Library. Prinzenstr. 1, D-3400 Göttingen, FR Germany.

RICHARD L. SMITH, President. Wei T'o Associates, Inc. 224 Early Street, Park Forest, IL 60467, U.S.A.

CONSULTANT EDITORS:

ABRAHAM ARAD, B.Sc., Chief of Restoration Section. Israel State Archives. Jerusalem, Israel.

EDMUND COLLINGS, Senior Lecturer. Camberwell School of Art and Crafts. Peckham Road, London SE5 8 UF, England.

IAN COOK, Principal Conservator. National Library of Australia, Canberra ACT 2600, Australia.

FRANÇOISE FLIEDER, Directeur du Centre de Recherches sur la Conservation des Documents Graphiques. 36 rue Geoffroy-Saint-Hilaire, F-75005 Paris, France.

YOMOKICHI IWASAKI, Director. 1-13-4 Ueno Sakuraghi, Taito-ku, Tokyo, Japan.

Y. P. KATHPALIA, M.Sc., Scientific Officer. National Archives of India. New Delhi 5, India.

ROMUALD KOSCIUSKO, Professor, Head of Microbiological Laboratory. Institute of Industrial Organic Chemistry. 1-23-236 Warsaw, Poland.

HELGA LUDWIG-SZKY, Chem.Eng., Chief of Restoration Department, Hungarian National Archives. Uri u. 54-56, H-1014 Budapest, Hungary.

FRANTIŠEK MARTINEK, Chief of the Department for Conservation and Restoration of Archival Material. Státní ústřední archiv v Praze. Karmelitská 2, 11801 Praha 1 – Malá Strana, Czechoslovakia.

I. P. MOKRETSOVA, Dr., VNIIR. 10, Krestyanskaya pl. SU-109172 Moscow, U.S.S.R.

ROBERT C. MORRISON, Lecturer. Canberra College of Advanced Education, School of Applied Science, Materials Conservation, P.O. Box 1, Belconnen ACT 2616, Australia.

YULIA PETROVNA NYUKSHA, Dr. (biol.sc.), Chief of the Department of Hygiene and Restoration of Books. M. E. Saltykova-Shchedrin State Public Library of Leningrad, SU-191069 Leningrad, U.S.S.R.

ENRICA ORMANNI, Direttore. Centro di fotoreproduzione, legatoria e restauro degli Archivi dello Stato. Via Constanza Baudana 14, I-00153 Rome, Italy.

JAN PIDEK, Head of Records Conservation Section. Public Archives. 395 Wellington Street, Ottawa K1A 0N3, Canada.

GALINA S. ROŽKOVA, Dr. (biol.sc.), Chief of the Department of Hygiene and Restoration of Books. State V. I. Lenin Library of the U.S.S.R., SU-101000 Moscow, U.S.S.R.

ANDRÉE SCUFFLAIRE, Dr.Phil. L., Conservateur. Archives Générales du Royaume, B-1000 Bruxelles, Belgium.

NORMAN J. SHAFFER, Chief of Photoduplication Service. Library of Congress. Washington. DC 20540, U.S.A.

CHANDRU J. SHAHANI, Ph.D., Chief of Document Preservation Branch. National Archives and Records Service. Washington. DC 20408. U.S.A.

RESTAURATOR, *International Journal for the Preservation of Library and Archival Material* is published quarterly. Annual subscription price is D.kr. 260.00 plus postage D.kr. 16.00 (total US\$ 34.00, £ 19.50, DM 83.00) payable in advance. Prices are subject to exchange rate fluctuation.

Subscription orders should be sent to MUNKSGAARD International Publishers, 35 Nørre Søgade, DK-1370 Copenhagen K, Denmark, or to any bookseller.

Microbiodeterioration of Library Materials

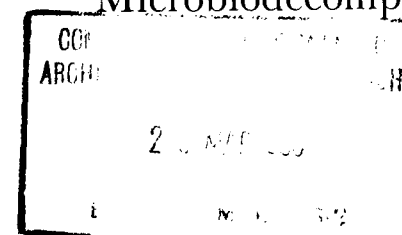
Part 2

Microbiodecomposition of Basic Organic

Library Materials

Chapter 4

By ROMUALD KOWALIK



CONTENTS

- 4.1.1 Decomposition of Textile by Microorganisms
- 4.1.2 Abstracts
- 4.1.3 References
- 4.2.1 Decomposition of Wood by Microorganisms
- 4.2.2 Abstracts
- 4.2.3 References
- 4.3.1 Decomposition of Papyrus by Microorganisms
- 4.3.2 Abstracts

- 4.3.3 References
- 4.4.1 Decomposition of Paper by Microorganisms
- 4.4.2 Abstracts
- 4.4.3 References
- 4.5.1 Decomposition of Parchment by Microorganisms
- 4.5.2 Abstracts
- 4.5.3 References
- 4.6.1 Decomposition of Leather by Microorganisms
- 4.6.2 Abstracts
- 4.6.3 References

4.1.1 Decomposition of Textile by Microorganisms

Textiles are made from the natural fibres of animal origin such as wool from the Bronze Age and silk, originated in China about 2000 B.C., and of vegetable origin such as linen, dated back as far as the Stone Age, as well as cotton, hemp, jute and sisal.

Flax has been grown in Sumer and in Egypt from very remote times and was used for the production of linen fabrics as early as the Neolithic period. The bronze statuettes from the time of Shulgi, Sumerian King dated 2100 B.C. in Ur, third dynasty, is covered probably by linen cloth (Iraq Museum). Linen cloth was found also in the tomb of Thutmose IV and in the tomb of Tut-ankh-Amun.

The home of the cotton industry is undoubtedly India. Cotton is mentioned in papyri as early as the second century. A.D.⁴³ The above mentioned vegetable fibres are composed of cellulose. Depending on the content of cellulose or lignin, material may be susceptible or resistant to microorganisms. Natural

cotton containing about 5% of noncellulosic products is less susceptible to microorganisms than flax, containing about 15% of noncellulosic products. Jute, which contains about 11% of lignin, is the most resistant because lignin possesses protective properties, and chemical removing of lignin destroys the resistance completely.⁵³

Animal fibres contain a nitrogenous compound-keratin. Although there are a very few instances of wool having been found in any tombs until a later date, there cannot be any doubt that the Sumerians and Egyptians made use of wool as a covering.

The agents, including catalysts, which cause deterioration of these materials are either biological, principal microorganisms (including bacteria, Actinomycetes and fungi) and insects (principally Coleoptera and sometimes other ones) and rodents. Also deteriorative agents may be of a physico-chemical nature, especially sunlight, oxygen, temperature changes, mechanical effects, and fire. Therefore, control of the museums' environment is becoming of prime importance.^{48, 52, 57, 58, 70}

The most serious damages in textiles are made undoubtedly by microorganisms. Wool fibres may be prone to attack by bacteria more easily than cotton fibres and less prone to attack by fungi.¹⁷ During wet weather *Bacillus subtilis*, *Bacillus mesentericus* and *Bacillus fusiformis* may cause deterioration of wool and fleece even before shearing.^{10, 17}

With silk, bacterial attack is more likely to take place before sericin has been removed rather than afterwards.

The Actinomycetes as was found are also serious agents of keratin decomposition.

The growth of four microorganisms in the presence of degreased wool fabrics was studied by some authors.²⁸ The species used were: *Bacillus mesentericus*, *Bacillus subtilis*, *Chaetomium globosum*, *Streptomyces albus*. This *Streptomyces* was the most active of the organisms tested, causing extreme deterioration of the wool fibres. After that it was also shown⁵¹ that *Streptomyces fradiae* decomposed the purified wool rapidly and completely. During this process soluble sulphydryl compounds accumulated in the cultures and the major nitrogenous product of decomposition was ammonia. *Streptomyces fradiae* also destroyed hair from sheep, cows and other animals due to keratinase production.³⁸ In the Indian tropical climate, deterioration of woollen fabrics is brought about by Actinomycetes, bacteria and fungi.¹ *Ctenomyces sp.* decrease the strength of woollen fabrics to the extent of 93% in 14 days⁶⁷ and according to Uniyal and others⁷² *Fusarium sp.*, *Aspergillus terreus*, *Aspergillus sp.*, *Aspergillus niger*, *Chaetomium sp.* and *Trichoderma sp.* were the prominent fungi isolated from wool in soil burial tests. During my stay in Egypt at the end of 1970 as a Unesco consultant it was

observed in the Greco-Roman Museum in Alexandria that the corduroy inside the showcases was completely covered with several species of fungi. Two species of fungi: *Trichoderma viride* and *Penicillium sp.* could be identified visually. The collection is threatened with such an infection because these fungi are difficult to combat. According to Dr. Daoud Abdo Daoud, custodian of the Greco-Roman Museum, the high relative humidity of Alexandria in July and August favours the development of biological agents.

Of special interests in connexion with the breakdown of keratin are dermatophytic fungi e.g. *Trichophyton* and *Microsporum* species, the ringworm organisms and *Candida albicans*, the yeast which causes thrush disease. There are parallels between the microbial attack on keratin and on collagen, the basic compound of parchment and leather.

The destruction of cotton textiles caused by microbial agency amounts to millions of dollars a year and considering economic importance, this problem is second only to wood deterioration. The evaluation of the deterioration of antique textiles and textiles utilized by libraries and archives seems to be impossible. Being cellulosic in composition cotton can be readily deteriorated by cellulose decomposing bacteria, Actinomycetes and fungi. Although there is evidence that bacteria may play an important role in the biological decomposition of cotton it is generally agreed that the fungi are the most active agents of deterioration. The most serious effect of microorganisms is the loss of strength, which can be completed in a few days in case of adverse conditions (damp, heat, lack of ventilation and contact with decaying matter). Besides losses of strength, staining can occur, due to pigmentation by the organisms or the reaction between products of its metabolism and finishes of the textile. Some microorganisms may use the cellulose itself, but there are many microorganisms that utilize other materials, which may be an easier assimilable source of food, as finishes, for example.

As has been said before, bacteria decompose, above all, keratinic fibres (wool, silk); cellulosic fibres, however, are destroyed by these microorganisms especially in damp environments or when buried in the soil. The most serious decomposition of cellulose is caused by species of *Sporocytophaga myxococcoides* and then by *Cellvibrio*, *Cellfalcicula*, *Microspora* and anaerobic *Clostridium*. Fungi and Actinomycetes destroy vegetable fibres abundantly, on animal fibres however they occur rarely. To the most important species of fungi, which destroy cellulose in textiles belong: *Chaetomium*, *Chaetomella*, *Myrothecium*, *Neurospora*, *Memnoniella*, *Stachybotrys*, *Fusarium*, *Mycogone*, *Stemphylium*, *Alternaria*, *Trichoderma*, *Cephalosporium*, *Trichocladium*, *Gliomastix*, *Sepedonium*, *Botryotrichum*, *Trichothecium*, *Stysanus*, *Scopulariopsis*, *Paecilomyces*, *Aspergillus* and *Penicillium*. On textiles occur sometimes *Mucor* and *Rhizopus*, which use carbohydrates and

Microbiodeterioration of Library Materials

nitrogen compounds.^{3, 4, 8, 9, 10, 15, 17, 18, 19, 24, 25, 28-31, 35, 36, 37, 38, 41, 47-51, 60, 61, 63, 64-69, 72, 76, 77}

Wood destroying fungi *Polyporus*, *Coniophora*, *Lenzites*, *Lentinus* take also some part in decomposition of textiles in field conditions. In museums wood destroying fungus *Merulius lacrymans* was observed too, especially on the carpets in badly ventilated store-rooms.

Deterioration of cellulosic textile by fungi is represented in Figs. 1 and 2.

Essential differences in the activity of particular microorganisms are based on the fact that bacteria and Actinomycetes need alkaline (pH = 6.8–8.0) and fungi acid medium. At the pH = 4.0 or less the fungi merely decompose cellulose of vegetable fibres. Fungi show, however, a great tolerance from nearly 1.0 to 9.5 of pH.

Much of the work during recent years in the field of biodeterioration of textiles has been concerned with fungi- and bactericides.^{1, 2, 4, 9, 10, 13, 14, 17, 19, 20-22, 24, 26, 27-30, 33, 34, 37, 39, 44, 46, 53-55, 58-60, 66-68} It is often said that there is at present no entirely satisfactory microbiocide. To be entirely satisfactory such a biocidal agent should be:

- a) toxic to a wide range of organisms or should block their action, and
- b) resistant to leaching;



Fig. 1. Deterioration of textile by fungi.

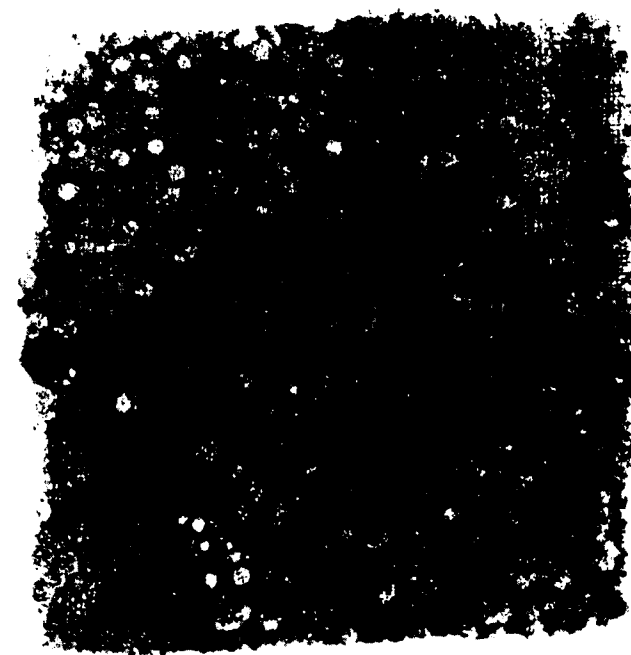


Fig. 2. Deterioration of textile by fungi.

and should not:

- c) be toxic to human beings,
- d) introduce undesirable colours,
- e) weaken the textile by reducing its tear strength,
- f) make the textile more sensitive to weakening by light.

Out of a great amount of biocides only a few may be selected for valuable objects. The best fungi- and bactericides seem to be phenols: *o*-phenylphenol, dichlorophene, salicylanilide, pentachlorophenol and its sodium and lauryl salts and dehydroabietylamine derivatives. This last compound is an excellent biocide in comparison to PCP laurate but it was not used commercially up to 1970.⁵³

Certain of the phenolic compounds have been used successfully over the years, particularly lauryl pentachlorophenate, sodium pentachlorophenate and *o*-phenylphenol. It is understandable that each biocide has advantages and disadvantages and we do not know the panaceum. Chlorophenols markedly accelerate the softening of cotton by sunlight. This defect can be overcome by incorporation of suitable screening agents.

From zinc compounds zinc naphthenate and zinc dimethyldithiocarbamate (low toxic, but according to the last reports recognized carcinogen) may be mentioned, and from tin compounds the best seems to be *tri-n*-butyl tin oxide. Zinc naphthenate and laurylpentachlorophenate provided protection against fungal deterioration at the jungle site in Nigeria.⁴⁴ Undyed wool can be preserved even at 100% R.H. in a closed container with *p*-dichlorobenzene crystals.¹⁰ *p*-Dichlorobenzene is known as insecticide. The book or books infested should be placed in the container and exposed to the vapours but not allowed to touch the crystals. According to Block^{9b} it is also effective in inhibiting the fungal growth in closed spaces. We have tried to examine *p*-dichlorobenzene as fungitoxicant by using food poisoning techniques. This compound is fungistatic against *Aspergillus terreus* Link (Fig. 3).

For textiles, protective agents may also be used.⁶⁶ Protective agents must be designed to poison microorganisms, to block their action by putting a protective layer over its food source, to change the source of good quality for microorganisms so that it can not be utilized.^{5, 6, 7, 12-14, 16, 20-23, 40-42} Most derivatives of cellulose exhibit a higher resistance to microbial attack. Treatments used have included acetylation, hydroxyethylation and carboxymethylation. Degree of substitution of minimum 1.0 is needed to inhibit decomposition of the cellulose.

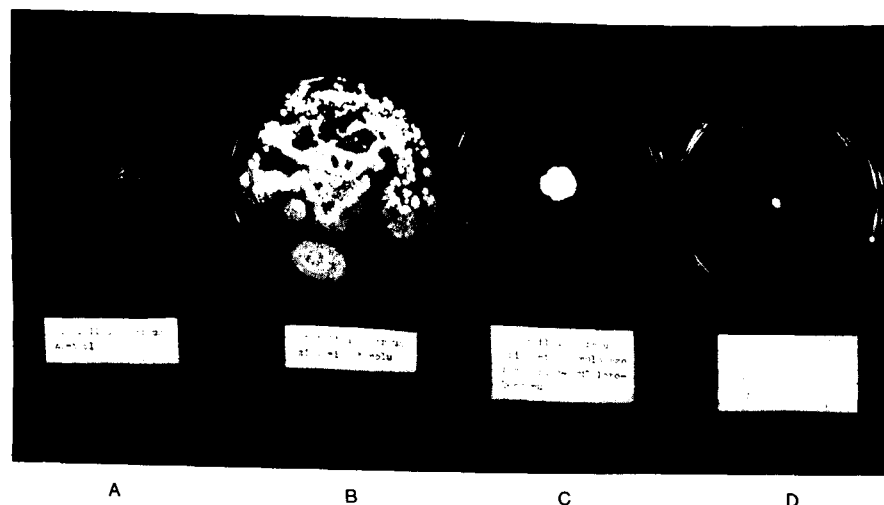


Fig. 3. Fungistatic activity of *p*-dichlorobenzene on *Aspergillus terreus*, Link.

- A. Control
- B. The activity of ethanol
- C. The efficiency of 10 g/m³ of *p*-dichlorobenzene
- D. The efficiency of 10 g/m³ of 4-chloro-3-cresol.

Inert barriers may also be introduced to protect cotton against microflora. Success in this field was achieved by impregnating the fabric with methylated trimethylolmelamine in the presence of cure/modifier/thiourea/ and an acid-forming catalyst.¹¹

In the Institute of Industrial Organic Chemistry in Warsaw from 5 kinds of cellulosic fibres on 17 different cellulosic media many fungi and Actinomycetes were isolated and identified. *Memmoniella echinata*, (Rivolta) Galloway described as characteristic for tropical countries was also isolated (Figs. 4 & 5).

It was found that ziram (zinc dimethyldithiocarbamate) or Shirlane (salicylanilide) together with a definite amount of methylolmelamine resin protected cellulosic textiles against microorganisms. Applied to impregnation, the resin formed a thin coating on the fibres and caused blocking of hydroxy group by reaction with cellulose. In this way hydrophilic character of fibres was decreased. Apart from that resin's polymerization, which takes place inside the fibres, develops cross linking between micelles and fibres and decreases swelling and water absorption particularly in amorphous areas. Besides that a toxicant is probably acting by combining with an important substrate to make that



Fig. 4. *Memmoniella echinata*, Rivolta Galloway, isolated from textile. (Magn. $\times 250$).



Fig. 5. *Memmoniella echinata*. (Magn. $\times 250$).

substrate no longer usable by enzyme or the whole organism. The enzyme inhibitor protects textile from attack by microorganisms.^{43a} This mechanism influenced negatively the growth of microorganisms and partly reduced the leaching of fungicides. The suitability of impregnation of cotton-wool and linen samples with fungistatic substances (ziram or Shirlane) and methylolmelamine resin for their protection against fungal attack was examined. Ziram combined with melamine resin was protecting even heavy fabrics not only in normal storage conditions, but also when stored in conditions favouring fungal growth.

Thin fabrics were protected almost as well by Shirlane.

Fungicidal activity of some fungicides-dichlorophen and Irgasan DP-300 and examples of textiles infected and protected by these fungicides are shown on Figures 6-15.

Some textile objects as in the Iraqi Museum or leather objects have been stained green with the products of corroded copper which have acted as a disinfecting agent during a long period of time. To the contaminated textiles in the Ethnographical Museum and in the National Museum of Wilanów 1% ethanol solution of 2,4,4'-trichlor-2'-hydroxydiphenylether (Irgasan DP-300) was used. Sometimes we were obliged to repeat the smearing of textiles, because resistant fungus as *Alternaria tenuis* was growing after the first treatment. Although *Alternaria tenuis* does not destroy cellulose intensely it may cause allergy in human beings. For the disinfection of graphic works of art we have proposed to use ethylene oxide with carbon dioxide in a vacuum chamber and afterwards the treatment with sodium chlorite (Figs. 16 & 17).

In 1962 a Polish draft proposal to determine the resistance of textile fabrics to fungal attack according to three methods was elaborated.⁷⁸

On the basis of *method A* it may be found if cellulosic fabrics will be affected by microorganisms decomposing cellulose slightly and existing only in the presence of other organic carbon sources. Apart from that it may be observed on impregnated fabrics if there exist any fungi which tolerate a high concentration of some fungicides or if tested fabrics contain soluble fungicides.

The experiments were performed on 100 mm Petri dishes on solid agar medium (10 g of agar, 10 g of oat meal, 20 g of malt extract and 950 ml of water). Agar medium is inoculated with popular fungi belonging to the species of *Penicillium* and *Aspergillus*. The evaluation of the results is made after two weeks of incubation at the temperature 26-30°C and 95% R.H.

On the basis of *method B* the degree of cellulose decomposition by the fungi occurring in different geographical latitudes including tropical countries is measured. The following species of fungi can be assessed:

Figs. 6-7. Fungicidal activity of dichlorophen and Irgasan DP-300 upon *Aspergillus terreus*, Thom.

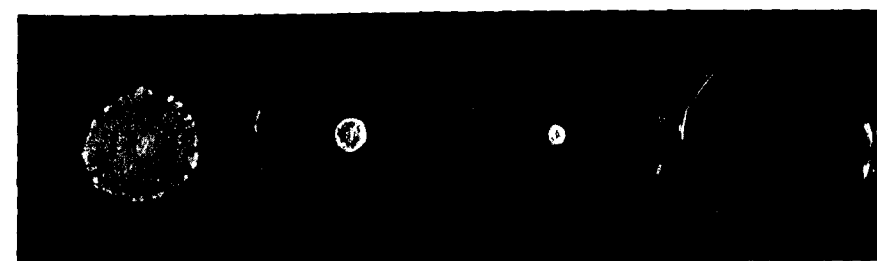


Fig. 6. Control 0,001 0,005 0,01
Concentration of dichlorophen in %.

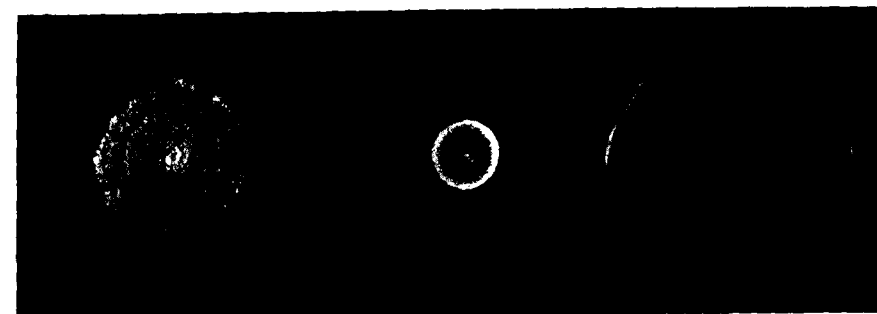


Fig. 7. Control 0,005 0,01
Concentration of Irgasan DP-300 in %.

Figs. 8-9. Fungicidal activity of dichlorophen and Irgasan DP-300 upon *Penicillium funiculosum*, Thom.

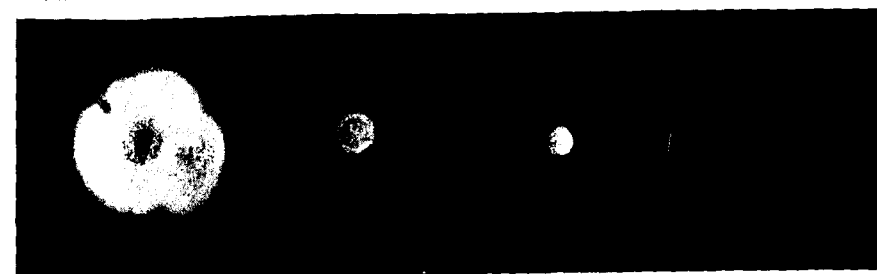


Fig. 8. Control 0,001 0,005 0,01
Concentration of dichlorophen in %.

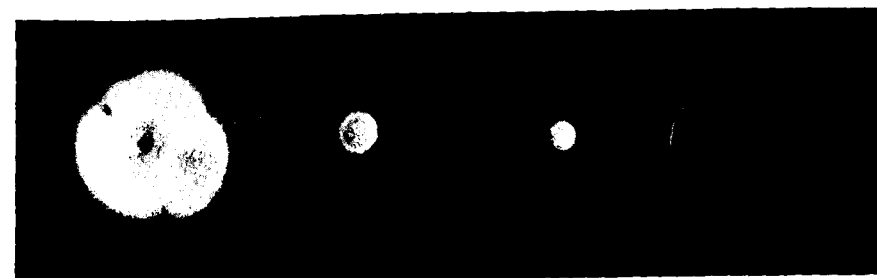


Fig. 9. Control 0,001 0,005 0,01
Concentration of Irgasan DP-300 in %.

Microbiodeterioration of Library Materials

Figs. 10–11. Fungicidal activity of Irgasan DP-300 tested immediately upon textile.



Fig. 10. Sample of textile smeared once of 1% ethanol solution of Irgasan DP-300.



Fig. 11. Sample of textile smeared twice of 1% ethanol solution of Irgasan DP-300.

Chaetomium globosum, Kunze

Myrothecium verrucaria, (Albertini and Schweinitz) Dittmar

Trichoderma viride, (Persoon) Harz, fungus which tolerates high concentration of sodium pentachlorophenate and other chlorinated phenols

Stachybotrys atra, Corda

Memnoniella echinata, (Rivolta) Galloway

Curvularia sp., Boedijn

Acrothecium sp., Preuss

Torula sp., Persoon

Paecilomyces varioti, Bainier

Aspergillus fumigatus, Fresenius

Penicillium funiculosum, Thom.

Penicillium tolerates high concentration of mercury, zinc and tin compounds. The tests are performed in 150 mm Petri dishes in solid medium of the following composition:

NH_4NO_3	3 g
MgSO_4	1 g
K_2HPO_4	0.3 g
KH_2PO_4	0.7 g
agar-agar	10 g
distilled water	1000 ml

Fig. 12. Samples of textile nonimpregnated and subjected during 14 days by *Myrothecium verrucaria* (Albertini and Schweinitz) Dittmar.



Fig. 13. Samples of textile impregnated with 1% of Irgasan DP-300 and subjected during 14 days by *Myrothecium verrucaria* (Albertini and Schweinitz) Dittmar.





Fig. 14. Samples of textile nonimpregnated and subjected during 14 days by *Chaetomium globosum*, Kunze.



Fig. 15. Samples of textile impregnated with 1% of Irgasan and subjected during 14 days by *Chaetomium globosum*, Kunze.

as well as traces of ZnSO_4 , CuSO_4 , FeSO_4 and MnSO_4 with filter paper discs of 120 mm diameter.

Medium is inoculated with spore suspension and incubated at 26–30°C and 95–100% R.H. After two weeks when fungi are sporulating, samples of textiles 10 × 150 mm are put on the discs of filter paper. Two weeks later the samples of textile are picked out and washed with water to remove mycelium, then they are air dried and kept in a desiccator. Tests to assess the mechanical properties of the samples are then carried out and the decrease of strength is determined according to the following equation:

$$H \text{ } 100\% - \frac{b}{a} \cdot 100$$

a = strength of control samples,

b = strength of samples after treatment with fungi.

Method C enables one to investigate the resistance of textiles in a soil burial test. In this case the conditions of testing are the most rigorous. Soil contains micro-organisms, which acting as individuals or collectively, decompose the most compounded organic structure to simple molecules. This test is carried out in standardized, biologically active soil.

The following composition of soil should be used:

- 1 part of composted soil,
- 1 part of well dispersed peat,
- 1 part of well decomposed manure,
- 1 part of gravel.

Composted soil should be 6 months old and mixed every two months. pH value of water extract of soil should range from 5.7–7.0. Activity of soil is assessed by burying the samples of cotton textile for 7–10 days in the soil. The samples should be destroyed by 80–100% after that time. The tested textiles are placed in a wooden box (height 150 mm) filled with the active soil for 4 weeks, in an incubator at the temperature 26–30°C and 85–95% R.H. After this time the strength of samples is determined, according to the above mentioned equation.

It was found⁴² that the most common fungus in soil is *Fusarium oxysporum* and this fungus together with *Sporotrichum pruinosum* and *Penicillium funiculosum* occur most often on textiles in the presence of different inhibitors. According to the experiments of Agarwal in India¹ soil burial tests cannot be treated as the sole method of assessing the inhibitors' influence, because in textiles which have no special treatment, the cellulolytic organisms start their attack right from the beginning without any hindrance. Hence there will be more damage by pure



Fig. 16. The work of art before conservation.

culture method as compared to the soil burial or the mixed culture method. The results in our laboratory confirm this supposition. In the case of soil burial the virulent cellulolytic fungi come into play only after the initial attack of bacteria and Actinomycetes and, therefore, the damage caused is not as rapid and severe as in a pure culture test. For the same reason the mixed culture and soil burial tests may prove better than pure culture tests when pretreated or sized textiles are used.

Wälchli^{73, 74} suggests using mixed culture as in nature and according to this author the use of fungi tolerating high concentration of tested fungicide is decisive for the test results.

4.1.2 Abstract

Decomposition of Textile by Microorganisms.

The survey, besides literature data, covers the results of 30 years work of the Microbiological Laboratory of the Institute of Industrial Organic Chemistry on microbial decomposition of val-



Fig. 17. The work of art after conservation and 1: Fumigation with ethylene oxide; 2: Treatment with sodium chlorite (according to Gettens system).

uable textiles. Some fungi and bacteria were isolated and identified. Fungi- and bactericides to protect textile materials were tested and some of them were used in practice in libraries and museums.

4.1.2 Résumé

Décomposition des textiles par action microbienne.

En plus de la présentation de données bibliographiques, l'exposé couvre l'ensemble des résultats de 30 années de travaux effectués par le Laboratoire de Microbiologie de l'Institut de Chimie Organique Industrielle, portant sur la décomposition microbienne de textiles de valeur. Certains types de moisissures et de bactéries ont été isolés et identifiés. Des fongicides et des bactéricides destinés à la protection des textiles ont fait l'objet d'essais, certains ont été utilisés en pratique dans les bibliothèques et les musées.

Microbiodeterioration of Library Materials

4.1.2 Resümee:

Zersetzung von Textilien durch Mikroorganismen.

Neben Literaturangaben enthält dieses Resümee die Ergebnisse der 30jährigen Tätigkeit des Mikrobiologischen Laboratoriums des Institutes für Industrielle Organische Chemie über die mikrobiologische Zersetzung wertvoller Textilien. Einige Pilze und Bakterien wurden isoliert und identifiziert. Fungizide und Bakterizide zum Schutz von Textilien wurden getestet, einige davon wurden in der Praxis in Bibliotheken und Museen verwendet.

4.1.3 References

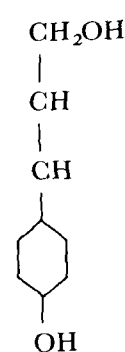
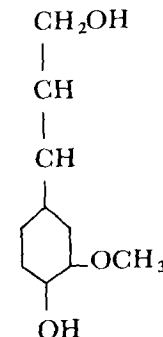
- Agarwal, P. N.: *Recent work on microbiological deterioration and its control*. Labdev Journal of Science and Technology 8B (3) (1970): 123–130.
- Anders, H.: *Organzinnverbindungen als Textilschutzmitteln*. Textil Praxis 16 (1961): 1.
- Baynes-Cope, A. D.: *The conservator's point of view*. Microbiological deterioration in the tropics. S. C. I. Monograph 23 (1966): 121–124.
- Becker, G.: *Biologische Untersuchung an Textilien*. Handbuch der Werkstoffprüfung 5 (1960): 971–1007. Berlin: Springer-Verlag.
- Beecher, E. R.: *The treatment of weakened fabrics*. The Museum Journal 58 (1959): 234–235.
- Bernard, W.: *Appretur der Textilien*. Berlin 1960: Springer-Verlag.
- Bellinger, L.: *Basic habits of textile fibres*. Rome Conference. Recent Advances in Conservation. London 1963: 192–196, Butterworths.
- Bhattacharya, J. R. & Basu, S. N.: *Detection of bacteria on jute and cotton by staining*. Textile Research Journal 36 (1966): 937–938.
- Block, S. S.: a. *Preservatives for Industrial Products* in Lawrence, C. A. (edit.). Disinfection, Sterilization and Preservation, Philadelphia 1968: 575–615, Febiger.
Block, S. S.: b. *Experiments in mildew prevention*. Modern Sanitation 3: (12) (1951): 61.
- Block, S. S.: *Fungicide as Industrial Preservatives* in Torgeson, D. C. (edit.). Fungicides I, 1967: 379–423, New York: Academic Press.
- Boyle, R. J.: *Rotproofing of cellulose fibers by a modified dry cure resin treatment*. Textile Research Journal 34 (1964): 319–324.
- Cooke, T. F.: *Resistance to microbiological deterioration of resin-treated cellulosic fabrics*. Textile Research Journal 24: (3) (1954): 197–209.
- Czerwińska, E., Kowalik, R., Pawłowska, Z.: *Mikrobiologiczne badanie oporności tkanin impregnowanych środkiem grzybobójczym i żywicznym melaminowym*. Acta Microbiologica Polonica 11 (1962): 383–392.
- Czerwińska, E., Kowalik, R., Pawłowska, Z.: *Badanie tkanin uodpornionych na gnienie*. In "Tworzywa Włókiennicze do Produkcji Ochron Osobistych". Centralna Rada Związków Zawodowych. Warszawa 1969: 184.
- Dingle, J. & Solomons, G. L.: *Enzymes from microfungi*. Journal of Applied Chemistry 2 (1952): 395–399.
- Discreus, L.: *Neue Verfahren in der Technik der chemischen Veredlung der Textilfasern*. Basel-Stuttgart 1953: Birkhäuser.
- Eddy, B. P.: *Microbial spoilage* in Rainbow, C., Rose, A. H. (eds.). Biochemistry of Industrial Microorganisms. New York 1963: 489–507: Academic Press.
- Galloway, L. D. & Burgess, R.: *Applied Mycology and Bacteriology* 1952: 45–75, London.
- Garnier, M. G.: *Aperçu de l'évolution des recherches en France concernant la protection des matériaux contre les agents biologiques de dégradation*. International Biodeterioration Bulletin 1 (1965): 27–29.
- Geijer, A. & Franzen, A. M.: *Textile grafund från Trondheims domkyrka*. International Institute of Conservation Abstract III (1960): 2638.
- Geijer, A.: *Preservation of textile objects*. Rome Conference. Recent Advances in Conservation. London 1961: 327–331: Butterworths.
- Geijer, A.: *Modocoll as a preservative for textile and other fragile objects*. Svenska Museer 1961: 1.
- Gérard, R.: *Restauration and conservation des drapeaux*. Archives Heraldiques Suisses 62 (1948): 53.
- Greathouse, G. H. & Wessel, C. J.: *Deterioration of Materials*. Causes and Preventive Techniques. New York 1954; Reinhold Publ. Co.
- Groom, P. & Panisset, T.: *Studies on Penicillium chrysogenum Thom in relation to temperature and relative humidity*. Annals of Applied Biology 20 (1933): 633–660.
- Haldenwanger, H. H. M.: *Biologische Zerstörung der Makromolekularen Werkstoffe*. Berlin 1970: Springer-Verlag.
- Hendey, N. J.: *Fungicidal efficiency of dichlorophene and PCP laurate*. Textile Manufacture 92 (1965): 45.
- Hirschman, D. J., Zametkin, J. M., Rogers, R. E.: *The utilization of wool by four saprophytic microorganisms in the presence of nutrient agents*. American Dyestaff Reporter 33 (1944): 353.
- Hueck, H. J.: *The biodeterioration of textiles and its prevention in Antiquities and Works of Art*, TNO Nieuws 20 (5) (1965): 301–307.
- Hueck, H. J.: *Textile pests and their control* in Leene, J. E. (edit.) Textile Conservation. London 1972: 76–97: Butterworths.
- Husemann, E.: *Macromolecular compounds. Degradation of cellulose and cellulose derivatives by means of acids, enzymes and oxidation*. Chemical Abstracts 48 (1954): 98–57.
- Husemann, E., Löss, E., Lötterle, H.: *Über den Fermentativen Abbau von Polysacchariden. II. Die Bestimmung der Aktivität von Cellulose, Xylanase und Mannanase*. Makromolekulare Chemie 6 (1951): 163–173.
- Ingham, R. K., Rosenberg, C. D., Gilman, H.: *Organotin Compounds*. Chemical Reviews 50 (1960): 459–539.
- Kerk, van der G. J. M.: *Quelques recherches dans le domaine de composés de l'étain*. Chimie et Industrie 90 (1963): 251–258.
- Kohlmeier, J.: *Über den Cellulose-Abbau durch einer phytopathogener Pilze*. Phytopathologische Zeitschrift 27 (1956): 147.
- Kowalik, R. & Czerwińska, E.: *Mikroorganizmy niszczące tkaniny wełniane i bawełniane*. Acta Microbiologica Polonica 5 (1956): 291–294.
- Kowalik, R. & Czerwińska, E.: *Wybrane zagadnienia mikrobiologii technicznej*. Podstawowe Problemy Współczesnej Techniki. Warszawa 1971: 17–67; Polska Akademia Nauk.
- Kuczajewa, A. G., Taptykowa, S. D., Gieszewa, R. L., Krassilnikow, N. A.: *Dokłady Akademii Nauk* 148 (1963): 1400.
- Lee, S.: *Laundry resistant antimildew proofing*. American Dyestaff Reporter 39 (1950): 145–151, 156.
- Leene, J. E.: *Restoration and preservation of ancient textiles and natural science*. Rome Conference. Recent Advances in Conservation: London 1961: 332– : Butterworths.
- Leene, J. E. (edit.). Textile Conservation: London 1972; Butterworths.
- Lloyd, A. O.: *The evaluation of rot resistance of cellulose textiles* In Walters, A. H. & Elphick, J. J. (eds.). Biodeterioration of Materials, Amsterdam-London-New York 1968: 170–177: Elsevier Publ. Co.
- Lucas, A. & Harris, J. R.: *Ancient Egyptian Materials and Industries*. London 1962: E. Arnold.

Microbiodegradation of Library Materials

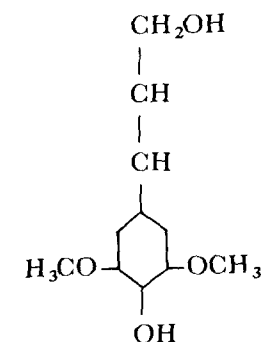
- 43a. Lukens, R. J.: Chemistry and Fungicidal Action. Berlin-Heidelberg-New York 1971: Springer-Verlag.
44. McNulty, B. J.: The testing of materials against fungi and termites. In SCI Monographs 23 (1966): 135-160: London.
45. Marsh, P. B., Bollenbacher, K., Butler, M. L., Guthrie, L. R.: S factor, a microbial enzyme which increases the swelling of cotton in alkali. Textile Research Journal 23 (1953): 878-888.
46. Marijnissen, R. H.: Degradation, Conservation, Restauration de l'Oeuvre d'Art, Brussels vol. I and II (1967): Arcade.
47. Nopitsch, M.: Wollschädigung durch Mikroorganismen. Melliand Textilberichte 25 (1946): 243-146.
48. Nopitsch, M.: Ursache und Bekämpfung von Schimmelbefall auf Textilien. Melliand Textilberichte 31 (1950): 619-627.
49. Nopitsch, M.: Die Beeinflussung bakterieller Schäden und Spinnstoffen durch Schweiß. Melliand Textilberichte 28 (1947): 161-164.
50. Nopitsch, M.: Bakterielle Schäden an Textilien und ihre Verhütung. Melliand Textilberichte 32 (1951): 344-346.
51. Noval, J. J., Nickerson, W. J.: Decomposition of keratin by microorganisms. Journal of the Society of Dyers and Colourists 76 (1960): 130.
52. Organ, R. M.: Design for Scientific Conservation of Antiquities. London 1968: Butterworths.
53. Parsons, H. L.: Rotproofing in relation to heavy textiles. Journal of the Society of Dyers and Colourists 86 (12) (1970): 504-512.
54. Pawłowska, Z., Czerwińska, E., Kowalik, R.: Determination of impregnated fabrics resistance against microorganisms. Chimie et Industrie 92 (1964): 3-bis.
55. Pawłowska, Z., Czerwińska, E., Kowalik, R.: Détermination de la resistance des tissus imprégnés vis-à-vis des microorganismes. Chimie et Industrie 94: (4) (1965): 370-375.
56. Pigman, W.: Cellulases, hemicellulases and related enzymes. The Enzymes 1 (1951): 725: New York.
57. Plenderleith, H. J.: The Conservation of Antiquities and Works of Art. London 1957: Oxford University Press.
58. Price, J. W.: Organotin compounds in pest control. Pest Technology 2 (1960): 66-69.
59. Ralph, R. S.: Rotproofing, mouldproofing and insectproofing with Mystox (LCPC). Catomance Leaflet No. 17.
60. Reese, E. T. (edit.): Advances in Enzyme Hydrolysis of Cellulose and Related Materials. Oxford 1963: Pergamon Press.
61. Reese, E. T. & Gilligan, W.: Separation of components of cellulolytic systems by paper chromatography. Archives of Biochemistry and Biophysics 45 (1953): 74-82.
62. Rawlins, F. Y. G.: The care of works of art. Research 11 (1958): 3-6.
63. Rogers, A. L.: Isolation of keratinophilic fungi from soil in the vicinity of Bogota, Colombia. Mycopathologia et Mycologia Applicata 44: (3) (1971): 261-264.
64. Rushmeyer, O. R. & Schmidt, E. L.: Cellulose decomposition in soil buried beds. II. Cellulolytic activity as influenced by alteration of soil properties. Applied Microbiology 6 (1958): 115-120.
65. Schmidt, E. L. & Rushmeyer, O. R.: Cellulose decomposition in soil buried beds. I. Soil properties in relation to cellulose degradation. Applied Microbiology 6 (1958): 108-114.
66. Selby, K.: The biodeterioration of cotton textiles and its prevention. In Microbiological Deterioration in the Tropics. SCI Monographs 23 (1966): 201-207.
67. Sen Gupta, S. R., Nigam, S. S., Tandan, R. N.: A new wool-destroying fungus *Ctenomyces* sp. Textile Research Journal 20 (1950): 671-673.
68. Siu, R. G. H.: Microbial Decomposition of Cellulose. New York 1951: Reinhold Publishing Co.
69. Thaysen, A. C. & Bunker, H. J.: The Microbiology of Cellulose, Hemicelluloses, Pectin and Gums. Oxford 1927: Oxford.
70. Thomson, G.: Textiles in the Museum environment in Leene J. E. (edit.) Textile Conservation, London (1972): 98-112: Butterworths.
71. Toishi, K., Toshiko, K., Rikuo, I.: Fading of dyed cloth and some attempts and its prevention. Scientific Paper of Japanese Antiquities 16 (1959): 19-26.
72. Uniyal, B. P., Chandran, R. B., Divekar, P. V.: Microbial degradation of wool. Technical Report India 50 (1966): 66.
73. Wälchli, O.: Bestimmung der Verrottungsbeständigkeit von Textilien in Erdbegrabungsversuch. Prüf-vorschrift 7 (1961): 11: Saint Gallen.
74. Wälchli, O.: Über den Einfluss verschiedener Versuchsanordnungen bei der Prüfung der Widerstandsfähigkeit von Textilien gegen Zelluloseabbauende Pilze. Material und Organismen 1 (2) (1965): 81-94.
75. Wälchli, O.: Biodeterioration Test Methodology In Walters, A. H. & Elphick, J. J. (eds.). Biodeterioration of Materials. Amsterdam-London-New York (1968): 242-251: Elsevier Publishing Co., Ltd.
76. Whitaker, D. R.: Purification of *Myrothecium verrucaria* cellulose. Archives of Biochemistry and Biophysics 43 (1953): 253-268.
77. White, W. L., Mandels, G. R., Siu, R. G. H.: Fungi in relation to the degradation of woolen fabrics. Mycologia 42 (1950): 189-199.
78. Polska, Norma PN-63 (P-04730 and P-04731): Wyznaczanie oporności tkanin z włókien celulozowych na działanie mikroflory. Warszawa (1963): Państwowy Komitet Normalizacyjny.

4.2.1 Decomposition of wood by microorganisms

From the chemical point of view wood is composed above all from lignin, the structure of which is not exactly known to date. The most famous authors such as Adler,¹ Brauns and Brauns,⁴ Freudenberg,¹¹ and Larsson and Miksche¹⁷ propose a structure of lignin. It is undoubtedly one of the most complicated, highly branched, irregular, three-dimensional, biopolymers, comprised of oxyphenylpropane units derived from three substituted cinnamyl alcohols: *p*-coumaryl, coniferyl and sinapyl alcohols.²³

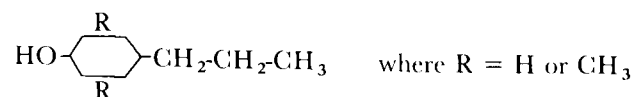
*p*-coumaryl alcohol

coniferyl alcohol



sinapyl alcohol

According to Sigleo²⁷ lignin is a complex of three-dimensional phenylpropane derivative



As is known lignin components of six species of wood are 4–10 times more resistant than cellulose components.⁶ Beside lignin the most important component of wood is cellulose, hemicelluloses, pectins and others, and because lignin exists in close association with these polymers, it limits the extent of utilization of these compounds.^{16a} It is interesting to microbiologists because it acts as a barrier to efficient bioconversion of lignocellulosics, as wood.

Kept under proper conditions wood is an exceptionally durable material, and wooden objects have been recovered after thousands of years from Egyptian tombs¹⁹ still in a perfect state of preservation, for instance a solar boat recovered near the pyramids in Gizeh.

Even in the damp climate of Northern Europe there are many wooden roofs that have stood for centuries without suffering the least deterioration; and our homes and museums contain innumerable pieces of furniture, hundreds of years old, which are as strong and serviceable to-day as on the day they were made. According to Borgin³ wood is probably a material which inherently is more stable than any synthetic organic structural polymer, because this material has survived for very long periods of time in widely differing types of environment from the mountainous climate of Norway to the dry climate of Arabic countries.

Wooden antiques such as furniture or carvings which have been kept, for instance, under whimsical Iraqi and dry Egyptian conditions are more or less seriously weakened by woodworms. More rarely, in countries of old civilizations, wooden objects may be found under water, where above all microorganisms are responsible for their deterioration. If wood is kept in damp conditions for any length of time it becomes seriously infected with wood-rotting fungi, which bring about its decomposition. Although several reports of bacterial degradation of the lignin polymer are found in the appropriate literature, lignin degradation appears to be primarily a fungal activity^{16a} and thus explains the biodegradation of this usually bio-resistant compound.⁶

Many important wood-destroying fungi belong to the group known as Basidiomycetes. Fungi capable of decomposing wood occur also in another large group of the higher fungi known as the Ascomycetes. Most of the fungi, which cause the troublesome dark stains in light coloured wood, belong to this group.

In practice, moisture content is the most important factor controlling the development of fungi on timber, as also on many other organic products. Fungi can develop on such materials only when they contain sufficient moisture. For the germination of the spores it is generally necessary not only for the substratum to be moist, but also for the relative humidity of the surrounding atmosphere to be high. Timber always contains a certain proportion of moisture unless it finds itself in a drying oven, or in a desiccator. The amount of moisture which it contains depends on the degree of saturation of the air (on the relative humidity) of the surrounding atmosphere.

Wood-rotting Basidiomycetes fungi flourish best in timber containing between 35% and 50% moisture.²⁵ There is no exact upper limit of moisture content for the growth of fungi in wood. The critical point is reached when the cell spaces are completely filled with water, for then there is no air in the wood, which is essential for the fungal growth. Fungal spores do not germinate readily on wood below 27–28% of moisture, but as a result of the chemical decomposition of wood by fungi a certain amount of moisture is produced from cellulose molecules, accelerating in this way the process of decomposition.

Most fungi need some air for their growth for the oxidation of the polymers, which they use for their growth and supply of energy. During respiration fungi produce carbon dioxide, which may accumulate in waterlogged wood and check the growth.

Fungi liquefy food materials by the secretion of enzymes by the walls of their hyphae and hydrolyse the biopolymers into glucose, which is absorbed. Wood-rotting fungi which decompose cellulose cause darkening of the wood. Other fungi in addition break down the lignin and cause the wood to become paler and reduce it to a fibrous mass. Wood which softens by decay may be eaten by wood-boring insects.

Out of the fungi the most prevalent in Europe and probably in other parts of the world are dry rot fungus *Merulius lacrymans* and the cellar fungus *Coniophora cerebella* and to a certain degree *Polyporus vaporarius*. *Merulius lacrymans* cause the so called “dry rot” and the cost of repairs of buildings in Central Europe affected by this fungus after World War II was estimated in hundreds of millions of dollars. As a result of these harmful organisms the wood becomes light in weight and friable. *Merulius lacrymans* thrives best in humid unventilated places where the air is quite still and the woodwork is damp but not saturated. On the surface of white mycelium of this fungus appear glistening drops of liquids. Afterwards tinges of pinkish lilac develop and here and there bright lemon yellow patches. Thick strands which soon appear can penetrate through masonry and brickwork and these strands are difficult to eradicate.¹⁰

Microbiodeterioration of Library Materials

Woods vary greatly in their natural durability when used under conditions conducive to decay. Some woods such as oak, teak and others have a high natural resistance to microbiological decay and will remain serviceable for many years. The sapwood however of practically all species is perishable.

The damage of wood is caused due to the action of the so called soft rot, for example, particularly by *Aureobasidium pullulans*, which reduces the aesthetic appearance of timber. *Cladosporium herbarum*, *Chaetomium globosum*, *Alternaria tenuis*, *Stemphylium verruculosum*, *Trichoderma viride* and *Torula* may cause the disfigurement of timbers.⁸ *Aureobasidium pullulans* causes depolymerization of the carbohydrates and 7% of cellulose and 3–4% loss in hemicelluloses. It was suggested that UV light may produce on wood surface a cellulose-rich zone, which assists the growth of the fungus. However Rösch and others²⁶ have demonstrated that *Aureobasidium* shows the presence of cellulose-polygalacturonase, -pectinoesterase, and -laccase activity indicating that it is capable of attacking carbohydrate directly in lignified cell walls. According to Dickinson⁸ preweathering of the surface is not necessary for the growth of *Aureobasidium pullulans*. After 18 months the timber varnish surface was so badly deteriorated that restoration would have been extremely difficult.

In addition to soft rot, brown rot and white rot fungi, wood may be damaged by bacteria.¹³ Bacterial cleavage occurs in lignin between phenylpropan units and *Pseudomonas acidovorans* used arylglycerol- β -aryl ether bond of lignin, as the sole source of carbon and energy. A characteristic odour of guajacol and vanillic acid were identified by Crawford and others.⁶ Bacteria have in general a lower and more restricted lytic activity than fungi, which make cell wall deterioration a prolonged process. In most of the wood colonising bacteria the pectinase has been found. Many wood-inhabiting bacteria also possess cellulase, thus being able to deteriorate cellulose, whereas the lignin content of the cell wall has a protective influence against these organisms. Some bacteria are apparently able to destroy also the lignified cell wall. This applies especially to wood after long exposure under wet conditions like archaeological wood. The depolymerization of the cell wall material follows as a direct erosion by bacteria.

In order to give the wood materials protection or resistance against those harmful wood destroying agencies, suitable preservatives seem to be needed.

In the last scores of years, a great amount of fungicides destined to protect wood were proposed. An ideal preservative for the protection of valuable wooden materials would be:

- toxic to wood-destroying microorganisms,
- chemically stable,

resistant to exudation, evaporation and volatilization of the active ingredients,
capable of good penetration.

In addition it would not:

- be corrosive to metals,
- render the wooden objects more flammable,
- adversely affect the strength, shape and finish of the wooden objects,
- have an objectionable smell,
- adversely affect the subsequent application of paint,
- be harmful to human beings and environment.

From the list of fungicides, museum and library keepers may select only a few.

From inorganic compounds:

		Concentration
Zinc chloride	ZnCl ₂	4%
Sodium fluoride	NaF	
Ammonium fluoride	/NH ₄ / ₂ F ₂	0.07-2%
may be used together with dinitrophenol		
Zinc silicofluoride	ZnSiF ₄	
Magnesium silicofluoride	MgSiF ₄	10%
Sodium silicofluoride	Na ₂ SiF ₄	
Ammonium silicofluoride	NH ₄ HSiF ₄	

Besides these, mercuric chloride HgCl₂ is still used; it penetrates to the depth of 2 cm and is used together with fluoride or dinitrophenol.

It is worth mentioning that out of inorganic microbiocides

borax and boric acid	Na ₄ B ₄ O ₇ and H ₃ BO ₃	1–2%
----------------------	---	------

have shown good effectiveness against wood-destroying fungi.

The discrepancy of these fungicides is believed to be due to the lack of resistance to leaching, but this characteristic is less essential when protecting the valuable objects. These chemicals are ingredients of several formulations for decreasing the flammability of wood, and their fungitocity and low toxicity to man³⁰ is believed to be an additional advantage. They do not adversely affect the subsequent application of paint and varnish. They are especially effective

Microbiodegradation of Library Materials

mixed with the well known organic compound pentachlorophenol^{5, 12, 22, 28} having however several disqualifying characteristics. Pentachlorophenol, besides being toxic, is weakly acidic and, under the influence of light, gives, besides hydrochloride, a red product chloranilic acid and other pigmented products. Moreover in commercial preparation of pentachlorophenol dibenzodioxins have been found. Dibenzodioxins are harmful on rat liver at the concentration of 20 and 100 ppm of technical pentachlorophenol,¹⁵ but, purified, was not harmful at this concentration.

In different works of art made of wood, the following organic compounds:

- Xylamon Combi light
- Xylamon BV special based on chloronaphthalin
- and Xylamon LX

have been used²⁹ in Europe, Japan and Nepal. These compounds are, however, rather insecti- than fungicides.

Mention should be made also of tin compounds and especially of *tri-n-butyl* tin oxide, but I agree with O'Neill and Skinner²⁴ that these compounds are not effective in wet and tropical conditions. Yoshikadzu³¹ however, who used an ethanol solution of *tri-n-butyl* tin oxide against *Aspergillus candidus*, *Aspergillus nidulans*, *Aspergillus versicolor*, *Oospora* sp., *Penicillium citreo-viride* and *Penicillium decumbens* in 1962 has observed that this treatment has been effective for ten years. Organo-tin-compounds are sometimes used together with silicone resins for the control of algae and mosses. Also

	Concentration
trichlorophenol	
sodium pentachlorophenate	0.1–0.3%
2.3-dichloro–1.4-naphthoquinone	
and quarternary ammonium compounds	

kill algae and mosses.

In our laboratory the activity of ethylene oxide and carbon dioxide on wood-destroying fungi *Coniophora cerebella* (Fig. 18), *Poria vaporaria*, *Serpula lacrymans* and *Polystictus versicolor* was tested. Fungi were cultivated in Kolle flasks on agar medium.

Microorganisms were incubated for three weeks at a temperature of 24°C and 88% R.H. After this period of time sterilized pine blocks measuring 5 × 2.5 × 1.5 cm were placed on the surface of mycelium and were incubated at the same conditions for 4 weeks. After these 4 weeks, blocks with vigorous growth

of fungi were removed and placed in sterilized Kolle flasks but without agar medium and were exposed to a gaseous mixture in a vacuum chamber for 4 hours, 8 hours and for 4 hours for two successive days. After treatment the blocks were placed on a freshly prepared agar medium and incubated for 3 weeks. It was observed that the fungi exposed after vigorous growth for 4 hours for two successive days were completely killed. After 8 hours exposure the growth of *Poria vaporaria* was observed, and samples exposed only to the vacuum effect and exposed for 4 hours grew on the agar medium similar to control flasks. As has been shown ethylene oxide used with carbon dioxide in a vacuum chamber for 4 hours for two successive days inhibits completely the growth of all tested wood-destroying fungi.

As may be seen from the experiments the evaluation of wood preservatives is a fairly complex subject. From the laboratory methods for evaluation of preservatives the agar block method is commonly used in Europe. The treated block

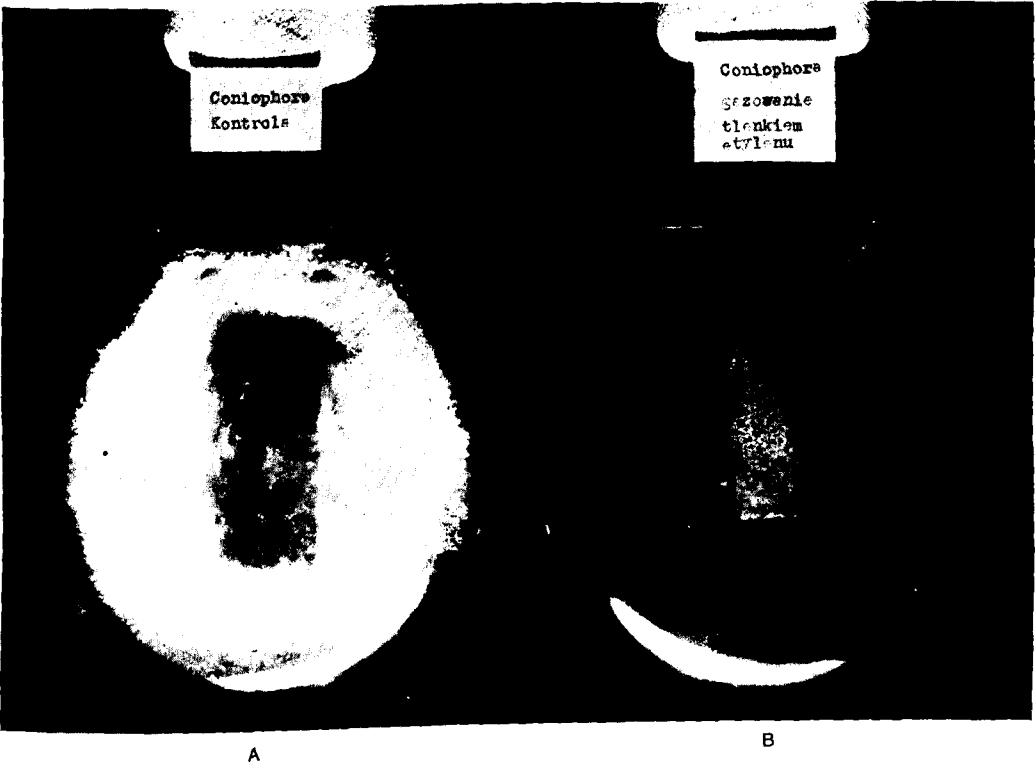


Fig. 18. Effect of ethylene oxide on wood-destroying fungus *Coniophora cerebella*.
A. Control
B. Vapour action of ethylene oxide for 4 hours for two successive days.

in this method is placed above a pure culture of a wood-destroying fungus growing on nutrient agar. Although soil is variable and complex and does not lend itself to precise and repeatable test techniques, it is the most hazardous environment for wood and it should be used in examining biodeterioration.¹⁴ The soil block method is standard in the USA. A strip of untreated wood called a feeder block is first placed on wet soil in a bottle and the entire assembly is steam sterilized. The feeder block is then inoculated with a pure culture and after a vigorous growth has developed the weighed treated block is placed on the decaying feeder block. After a fixed period of exposure, usually 12 weeks, the treated block is removed, conditioned to its original moisture content and again weighed. The loss in weight indicates the extent of decay. The minimum retention of a chemical required to prevent decay is designated as the threshold retention. The treated block may be subjected to artificial weathering in the laboratory before exposure to the fungus, thus providing an index of the preservative's permanence. This method was first described by Flerow and Popow in 1933 and it was developed independently in the USA by Leutritz.¹⁸ A modification of the standard soil block method gives a very interesting method in which the deformation of impregnated and unimpregnated wood under the influence of fungi is measured.

A new technique for screening fungicides on filter paper immersed in fungicide and measurement of fungus diameter for wood preservation (Fig. 19) has been given by Dickinson.⁹

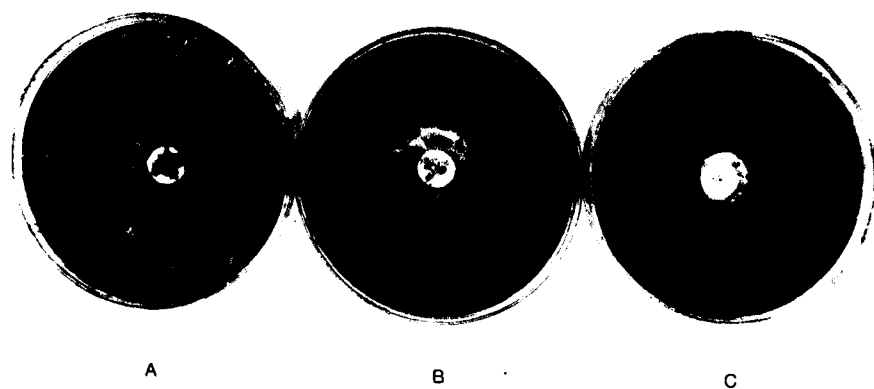


Fig. 19. Dickinson's screening test methods of wood-preserving fungicides-tin compounds.

- A. Control of *Coniophora cerebella*
 B. 0.005% of fungicide treated filter paper disc
 C. 0.01% of fungicide.

To develop a laboratory test for surface applied preservatives, which would be related to infection by air borne spores, *Lenzites trabea* was chosen as the most suitable fungus, but although it germinated readily on nutrient agar, moist cellophane, paper and thin sections of pine sapwood, it would not germinate on pine sapwood blocks.²

4.2.2 Abstract

Decomposition of Wood by Microorganisms

The chemical components of wood and its biodegradation by different fungi and bacteria, which utilize various biopolymers of wood were given. Some pesticides for the protection of valuable wood objects, as well as standard methods and other techniques for screening fungicides were proposed.

4.2.2 Résumé

Décomposition du bois par action microbienne.

Les substances chimiques du bois et leur biodégradation par différents types de moisissures et de bactéries utilisant divers biopolymères du bois ont été passées en revue. Certains pesticides servant à la protection d'objets précieux en bois, des méthodes standard et d'autres techniques de sélection de fongicides ont été proposées.

4.2.2 Resümee:

Zersetzung von Holz durch Mikroorganismen.

Angegeben wurden die chemischen Bestandteile von Holz und dessen biologischer Abbau durch verschiedene Pilze und Bakterien, die einige Holzpolymere verwerten. Weiterhin wurden eine Reihe von Pestiziden zum Schutz wertvoller Holzgegenstände sowie Standardmethoden und andere Verfahren mit Schutzfungiziden dargestellt.

4.2.3 References

1. Adler, E.: *Recent studies on the structural elements and the reactions of lignin*. In *Chimie et Biochimie. Lignine, Cellulose, Hemicelluloses*, Actes Symposium Internationale. Grenoble, France 1964: 73-83.
2. Baker, J. M., Miller, E. R., Morgan, J. W., Savory, J. G.: *Princes Risborough Laboratory Work 1972*. British Wood Preservers Association. Records of the 1973 Annual Convention 1973: 3-22.
3. Borgin, K.: *The inherent durability of wood*. British Wood Preservers Association. Records of the 1973 Annual Convention 1973: 105-126.
4. Brauns, F., Brauns, D.: *Chemistry of Lignin*. Academic Press. New York 1960.
5. Carswell, T. S. & Hatfield, I.: *Pentachlorophenol for wood preservation*. *Industrial Engineering Chemistry* 37 (1939): 1431-1435.
6. Crawford, D. L., Crawford, R. L., Pometto, A. L.: *Preparation of specifically labelled ¹⁴C-/Lignin/ and ¹⁴C-/Cellulose-/Lignocelluloses and their decomposition by the microflora of soil*. *Applied and Environmental Microbiology* 33: (6) (1977): 1247-1251.

7. Crawford, R. L., Kirk, T. K., Harkin, J. M., McCoy, E.: *Bacteria cleavage of arylglycerol- β -aryl ether bond*. Applied Microbiology 25: (2) (1973): 322–324.
8. Dickinson, D. J.: *Disfigurement of decorative timbers by blue stain fungi*. British Wood Preservers Association. Records of the 1971 Annual Convention 1971: 151–169.
9. Dickinson, D. J.: *A new technique for screening fungicide for wood preservation*. International Biodeterioration Bulletin 10: (2) (1974): 49–51.
10. Findlay, W. P. K.: *Timber Pests and Diseases*. Oxford 1967: Pergamon Press.
11. Freudenberg, K.: *Lignin, its constitution and formation from p-hydroxycinnamyl alcohols*. Science 148 (1965): 595–600.
12. Hatfield, I.: *How to paint over wood products that are pressure preserved with penta*. Wood Preserving News 39 (1961): 27–28.
13. Hedley, M. E. & Foster, J. B.: *Modified soil block technique for assessing wood decay*. New Zealand Journal of Forestry Science 2 (2) (1972): 237–248.
14. Hilditch, E. A. & Hambling, R. E.: *Wood Preservative Tests and other Assessment*. British Wood Preservers Association. Records of the 1971 Annual Convention 1971: 91–113.
15. Kimbrough, R. D. & Linder, R. E.: *The effect of technical and purified Pentachlorophenol on the rat liver*. Toxicology and Applied Pharmacology 46 (1978): 151–162.
16. Kirk, T. K. & Crawford, R. L.: *Effects of microorganism on lignin*. Annual Review of Phytopathology 9 (1971): 185–210.
- 16a. Kirk, T. K., Yang, H. H., Keyser, P.: *The chemistry and physiology of fungal degradation of lignin*. Development of Industrial Microbiology 19 (1978): 51–61.
17. Larsson, S. & Miksche, G. E.: *Gaschromatografische Analyse von Ligninoxidationsprodukte*. IV. Zur Struktur des Lignins der Birke. Acta Chemica Scandinavica 25 (1971): 647–662.
18. Leutritz, J.: *Acceleration of toxic tests of wood preservatives by the use of soil as a medium*. Phytopathology 29 (1939): 901–903.
19. Lucas, A. & Harris, J. R.: *Ancient Egyptian Materials and Industries*. E. Arnold Publication: London 1962.
20. Mateus, T. J. E.: *A mechanical test for studying wood preservatives (Lisbon)*. British Wood Preservers Association. Records of the 1957 Annual Convention. Cambridge 1957: 137–170.
21. Matsumura, F.: *Microbial Degradation of Pesticides with Particular Reference to the Formation of Terminal Residues*. Environmental Quality and Safety vol. 4 1975 Stuttgart: 160–174. G. Thieme Verlag.
22. Meyer, F. J. & Gooch, R. M.: *The effect of oil carriers on the performance of treated wood*. Forest Products Journal 6 (1956): 117–121.
23. Nicholas, D. D. (edit.): *Wood Deterioration and its Prevention by Preservative Treatments*. Syracuse University Press 1973, vol. I: 155.
24. O'Neill, L. A. & Skinner, C. E.: *Laboratory tests for resistance of paint films to mould growth under tropical conditions*. Society of Chemical Industry Monograph No 23 (1966): 170, London.
25. Roth, H. G.: *Climatic and structural conditions that favour attack by wood destroying fungi*. Pest Control 24: 1 (1956): 30–35.
26. Rösch, R., Liese, W., Berndt, H.: *Untersuchungen über die Enzyme von Bläue Pilzen. I. Cellulase-Polygalacturonase-Pectinesterase- and Laccase Aktivität*. Archiv für Mikrobiologie 67 (1969): 28–50.
27. Sigleo, A. C.: *Degraded lignin compounds identified in silicified wood 200 million years old*. Science 200 (4345) (1978): 1054–1055.
28. Sakornbut, S. S. & Merrill, H. L.: *Detection of pentachlorophenol in treated wood*. Analytical Chemistry 27 (1955): 1259–1261.
29. Steinberg, K.: *Wood Preservation and Art*. Bayer Reports 36 (1976): 41–45.
30. Weir, R. J. & Fisher, R. S.: *Toxicologic Studies on Borax and Boric Acid*. Toxicology and Applied Pharmacology 23: (3) (1972): 351–364.
31. Yoshikadzu, E.: *Fungi control for the statues of Yakushi/Bhaissayaguru/Triad the Hōjōbo Temple, Ischra. Kanagawa Prefecture*. Science for Conservation 9 (1972): 51–53.

4.3.1 Decomposition of Papyrus by Microorganisms

Papyrus as paper-like material used for writing purposes has been known from 2200–2000 years B.C.⁵ It is worth noting that the most ancient papyrus collections are the best quality. The papyrus sheets which have been manufactured in the last centuries B.C. seem to be thick and less elegant, although still good ones. After the third century A.D. however the quality of papyrus violently changes for the worse and papyrus from this time is similar to our cardboard. Independently from climatic conditions, which were not ideal to inhibit the growth of microorganisms (and excavators, for instance,⁷ continually complained of the damp foetid atmosphere present in the Tut-ankh-Amon tomb), pH played a significant role in the preservation of papyrus and we are aware that Egyptians used a form of sodium bicarbonate in mummification. Some of this material came into contact with the mummy papyrus wrappings with a resultant long term preservation of wrappings. Certain old papers manufactured in a limestone region owed their remarkable state of preservation to the presence of calcium carbonate.¹

Papyrus contains as a basis biopolymers related with the ones existing in paper. Papyrus however contains more lignin and less cellulose than paper. Above all, there exists an essential difference in the composition of these two writing materials. The only cementing material in papyrus as a rule is natural papyrus polymer consisting of galactose, arabinose and rhamnose without an extraneous adhesive,² though the individual sheets were subsequently stuck together, while paper sheets are sized, with starch, animal glue, resin and other materials. Therefore we have tried to compare these two materials, since we could not find any traces in the literature that microflora of papyrus have been studied before.³

Samples of papyrus were collected as well as cardboard in which papyrus was wrapped. These samples were placed in sterilized Petri dishes for further testing in the Cairo Centre of Research and Conservation of Antiquities and in the Microbiological Laboratory of the Institute of Industrial Organic Chemistry in Warsaw. To isolate microorganisms from papyrus, the method of impression as a rule was used. Sterilized filter paper discs were pressed to microflora stains, and then the discs were transferred to Petri dishes. With a sterile pipette

Microbiodeterioration of Library Materials

15 ml of liquid medium was poured into every 100 mm Petri dish with filter paper discs and sometimes with samples of papyrus. Owing to the great variations in the nutrient requirements of particular species or genres of microorganisms, their isolation was carried out by employing several cellulosic elective media.^{3, 4} I shall give the composition of these media, because we have used the same ones during isolation of microorganisms decomposing the paper. For part (500 ml) of each medium the pH of the solution was adjusted to 5.0–5.6, and for the other part (500 ml) to 7.0–7.5, in order to isolate the fungi, bacteria and Actinomycetes.

Medium of Greathouse, Klemme and Barker:

K ₂ HPO ₄	1.3940 g	CaCO ₃	0.005 g
MgSO ₄ ·7 H ₂ O	0.7395 g	Fe, Zn and Mn as SO ₄ salt	traces
NH ₄ NO ₃	1.006 g	distilled water	1000 ml

Medium of Greathouse, Klemme and Barker modified:

In the composition of this medium NH₄NO₃ was replaced by NH₄H₂PO₄. 1.3013 g of NH₄H₂PO₄ was used and the amounts of other components were left unaltered.

Medium of Rogers, Wheeler and Humfeld:

NaNO ₃	3 g
K ₂ HPO ₄	1 g
MgSO ₄ ·7 H ₂ O	0.25 g
KCl	0.25 g
running water	1000 ml

Medium of Hutchinson:

K ₂ HPO ₄	1 g
KCl	0.1 g
MgSO ₄ ·7 H ₂ O	0.3 g
NaCl	0.1 g
FeCl ₃	0.01 g
NaNO ₃	2.5 g
distilled water	1000 ml

Medium of Dubos:

K ₂ HPO ₄	1 g
KCl	0.5 g
MgSO ₄ ·7 H ₂ O	0.5 g
NaNO ₃	1 g
FeSO ₄ ·7 H ₂ O	0.01 g
distilled water	1000 ml

Medium of Winogradski:

KH ₂ PO ₄	1 g
MgSO ₄ ·7 H ₂ O	0.5 g
NaCl	0.5 g
FeSO ₄	0.01 g
MnSO ₄	0.01 g
KNO ₃	4 g
CaCO ₃	20 g added after adjusting of pH
distilled water	1000 ml

Medium of Fähræus:

NaNO ₃	0.2 g
K ₂ HPO ₄	0.1 g
MgSO ₄ ·7 H ₂ O	0.05 g
KCl	0.05 g
CaCl ₂ ·6 H ₂ O	0.02 g
FeSO ₄ ·7 H ₂ O	0.002 g
MnSO ₄ ·4 H ₂ O	0.002 g
distilled water	1000 ml

Medium of McBeth:

K ₂ HPO ₄	1 g
(NH ₄) ₂ SO ₄	2 g
MgSO ₄ ·7 H ₂ O	1 g
Na ₂ CO ₃	1 g
CaCO ₃	2 g
distilled water	1000 ml
pH was adjusted to	8.7

Medium of Van Iterson:

For fungi	
NH ₄ NO ₃	0.5 g
KH ₂ PO ₄	0.5 g
running water	1000 ml
pH was adjusted to	5.5

Medium of Stapp and Bortels:

For fungi	
(NH ₄) ₂ SO ₄	0.5 g
KH ₂ PO ₄	0.25 g
MgSO ₄	0.1 g
running water	1000 ml
pH was adjusted to	6.5 with H ₂ SO ₄
All previous media were adjusted with	HCl.

Medium of Omelianski:

(NH ₄) ₂ SO ₄	1 g
K ₂ HPO ₄	1 g
MgSO ₄ ·7 H ₂ O	0.5 g
NaCl	trace
CaCO ₃	added before use
distilled water	1000 ml

For bacteria

NH ₄ Cl	1 g
K ₂ HPO ₄	0.5 g
CaCO ₃	20 g
running water	1000 ml
pH was adjusted to	7.0

For bacteria

NaNO ₃	0.5 g
K ₂ HPO ₄	0.25 g
MgSO ₄	0.1 g
running water	1000 ml
pH was adjusted to	7.5 with NaOH
as in previous media.	

Identification of fungi and Actinomycetes was made by the examination of their morphology and their spore production, if necessary during about a dozen days of growth. For this purpose, small squares 1 × 1 cm prepared from transparent

viscose film were laid on a cotton wad impregnated with liquid mineral salts, as a rule Greathouse medium³ and these were placed in Petri dishes, sterilized and inoculated. In order to obtain thin transparent colonies a medium of 10% or even 1% of the usual strength was used. Single pieces of film were removed at intervals for examination of various stages of growth and for photography. Using these methods about 40 different microorganisms were isolated and identified. Some microorganisms such as *Alternaria* (Figs. 1, 2), *Botryodiplodia theobromae* (Figs. 3, 4), *Emericellopsis minima* (Figs. 5, 6), *Fusarium lactis*, *Helminthosporium sativum* (Figs. 7, 8), *Spondylocadium australe* (Figs. 9, 10) and some species of the genus *Chaetomium*, for instance *Chaetomium globosum* (Figs. 11, 12) and *Chaetomium dolichotrichum* (Figs. 13, 14) seem to be specific for papyrus and/or for Egyptian climatic conditions. *Actinomyces*, which were often isolated, participate also in the microbiodeterioration of papyrus. They do not grow as vigorously as fungi, but they are, better than other organisms, used to unsuitable conditions, such as lower relative humidity and they are endowed with their own defensive systems against bacteria, fungi and against chemical activity of toxic compounds.

Even in a very dry atmosphere for the growth of microflora, as the Sakkarah desert, the majority of material of the great libraries of ancient countries have disappeared primarily under the influence of microflora. Therefore some experiments upon cellulolytic activity of papyrus deteriorating microorganisms were carried out in our laboratory. It was observed that the genus *Chaetomium* may play a great role in decomposition of papyrus. The amount of cellulose decomposed by *Chaetomium globosum*, *Chaetomium ochraceum* and *Chaetomium elatum* ranged from 76.7 to 100%. The next fungus which may destroy papyrus severely is *Emericellopsis minima* and the amount of cellulose decomposed by this genus ranged approximately 77%.

Since the natural size in papyrus is a natural rubber, a polymer of galactose, arabinose and rhamnose,⁴ it was decided to study the possibility of these last sugars being used by 31 species of microorganisms isolated from papyrus. It was found that the majority of microorganisms may utilize these natural adhesives of papyrus as a carbon source. It is interesting that some fungi which slightly utilize sugars decompose cellulose intensely and these, which hydrolyze sugars intensely, decompose cellulose only slightly.

Hydrolysis of the basic components of papyrus initiated by fungi can take place when fungi have nitrogen above all at their disposal. Fungi may use nitrogen compounds from papyrus and from constituents of a polluted atmosphere. During the examination of nitrogen sources Greathouse medium containing ammonium nitrate was used. Ammonium nitrate was subsequently replaced by equivalent amounts of sodium nitrate, ammonium phosphate and



Fig. 1. *Alternaria geophila*, Daszewska ($\times 500$).

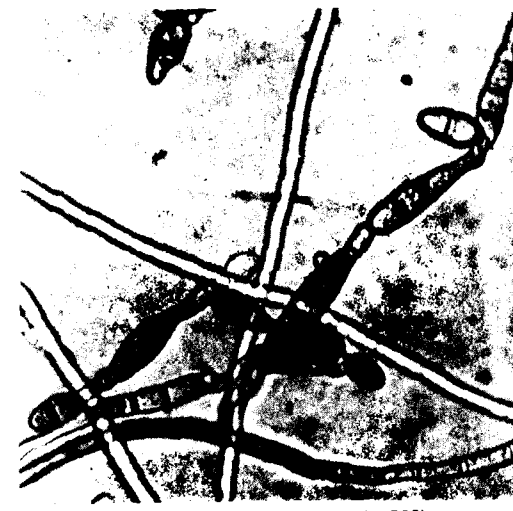


Fig. 2. *Alternaria geophila*, Daszewska ($\times 500$).

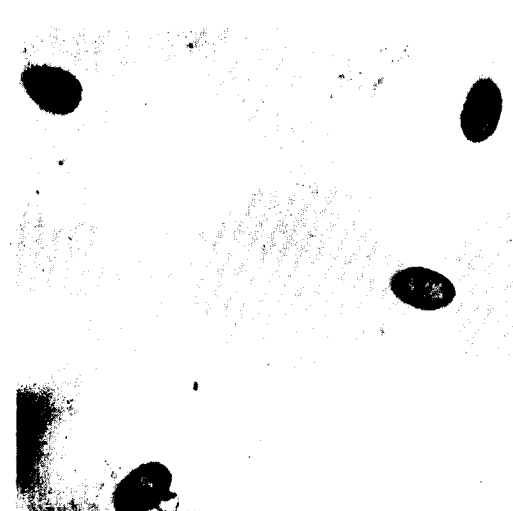


Fig. 3. *Botryodiplodia theobromae*, Patouillard. Spores ($\times 250$).

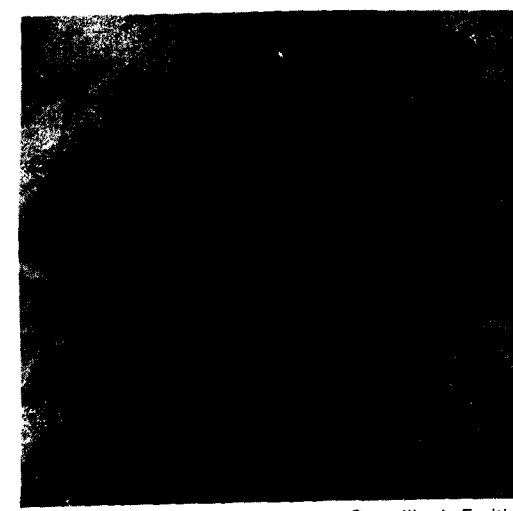


Fig. 4. *Botryodiplodia theobromae*, Patouillard. Fruiting body ($\times 250$).



Fig. 5. *Emericellopsis minima*, Stolk ($\times 250$).

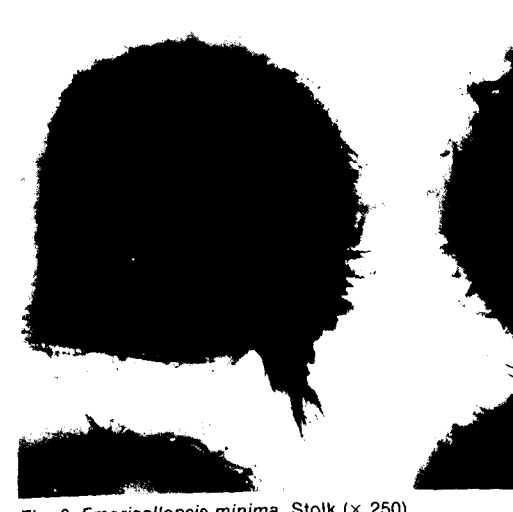


Fig. 6. *Emericellopsis minima*, Stolk ($\times 250$).



Fig. 7. *Helminthosporium sativum*, Pammel, King and Bakke ($\times 250$).



Fig. 8. *Helminthosporium sativum*, Pammel, King and Bakke ($\times 250$).



Fig. 9. *Spondylocladium australe*, Gilman and Abbott ($\times 250$).



Fig. 10. *Spondylocladium australe*, Gilman and Abbott ($\times 500$).

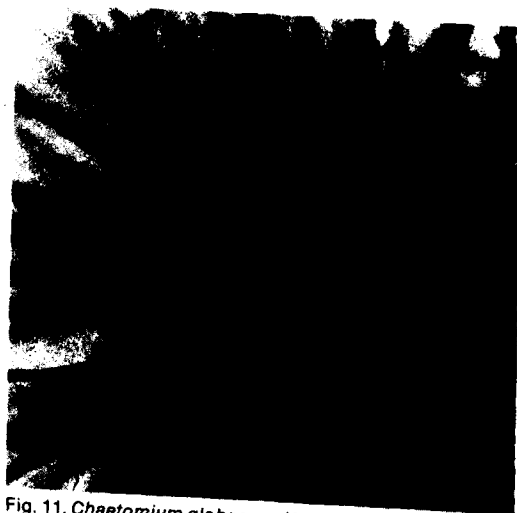


Fig. 11. *Chaetomium globosum*, Kunze. Young perithecium ($\times 250$).



Fig. 12. *Chaetomium globosum*, Kunze ($\times 500$).

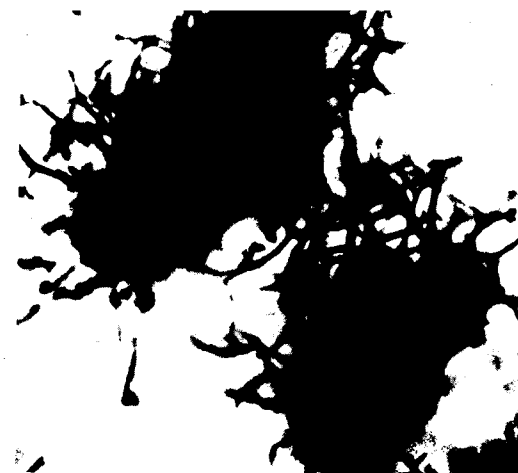


Fig. 13. *Chaetomium dolichotrichum*, Ames ($\times 100$).



Fig. 14. *Chaetomium dolichotrichum*, Ames ($\times 250$).

ammonium sulphate. The pH of the media was adjusted to 3.0; 4.0; up to 10.0.

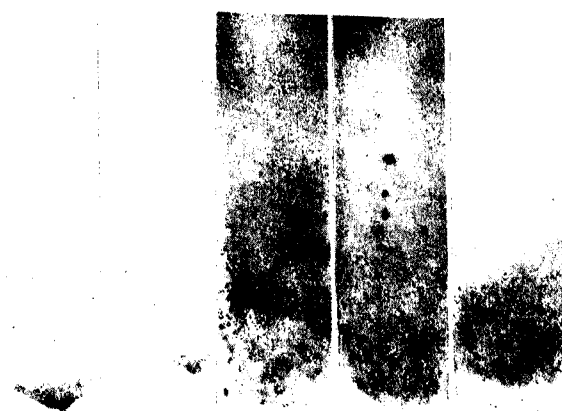
After 10 to 14 days of incubation, depending on the species of microorganisms, at 24–26°C and 95% R.H., filter paper strips were taken out from the glass tubes, placed over formaldehyde vapour for 24 hours and laminated with polyethylene foils in a laminator. They are illustrated on Figs. 15 and 16 for *Fusarium lactis*, Pirota and Riboni and for *Chaetomium globosum*, Kunze on Figs. 17 and 18.

It was found that papyrus destroying microorganisms preferred ammonium to nitrate ions. It was stated also that utilization of ammonium ions from three examined media was better at high pH, and nitrate was preferred at lower pH. Sometimes ammonium ion may be unsuitable or even toxic for some fungi as *Eidamella spinosa* and *Spondylocladium australe*, and they grow better on sodium nitrate.

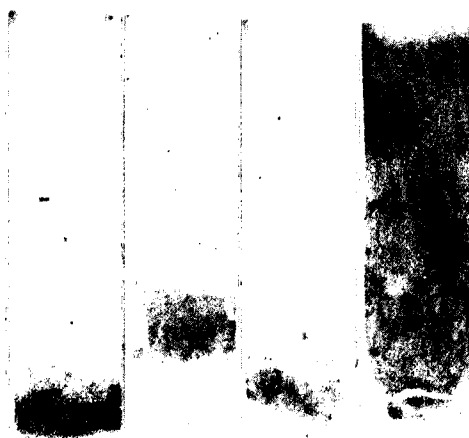
Spores of fungi are ubiquitous and they await only the proper conditions of moisture and temperature to grow and reproduce. Papyrus decomposing microorganisms may grow intensely as well at 24–26°C as at 30°C, and some of them also at a temperature of 42°C. It is interesting that the members of the genus *Penicillium*, which prefer rather low temperature and are frequent inhabitants of papers, were isolated from papyrus only once.

The tests to select microbiocides for the protection of papyrus were made too. Blotting paper impregnated with a 10% solution of particular biocide: pentachlorophenol, 2,2'-dihydroxy-5,5'-dichlorodiphenylomethane, 4-chloro-3-cresol and thymol was placed for a period of 7 days between paper sheets of a high lignin content. After that time strips measuring 110 $\times$ 20 mm were cut and put in Petri dishes on the surface of a mineralized agar medium of pH = 6.0. The strips were inoculated with spore suspensions of the three fungi: *Chaetomium globosum*, Kunze, *Aspergillus terreus*, Thom and *Stachybotrys atra*,

Fusarium lactis Pirotta and Riboni



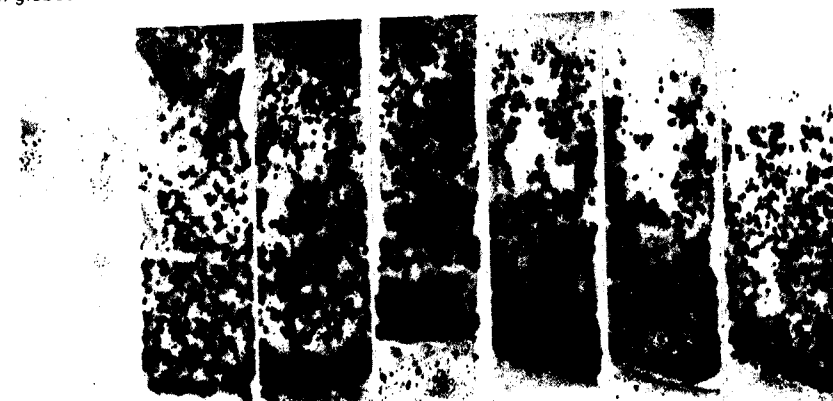
$\text{NH}_4\text{H}_2\text{PO}_4$ (pH = 3.0–10.0)



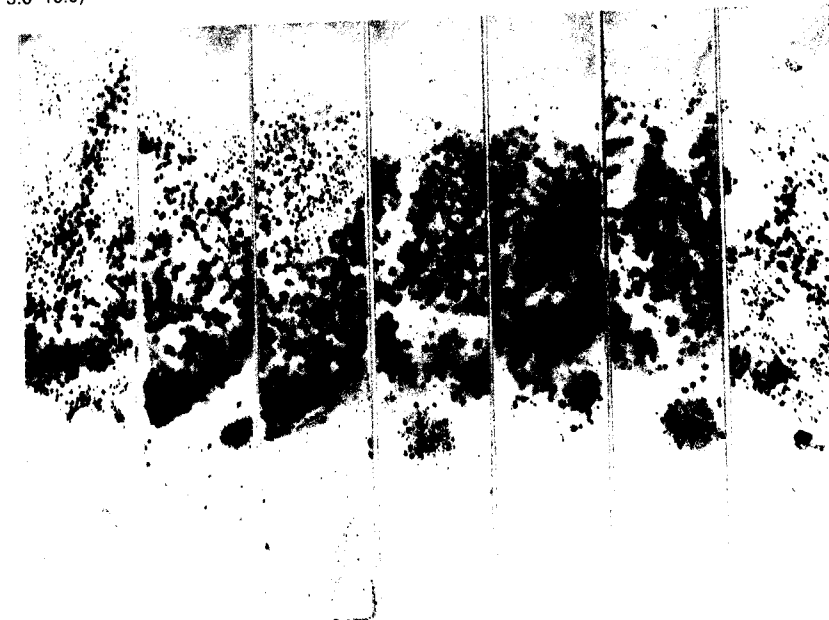
$\text{NH}_4/2\text{SO}_4$ (pH = 3.0–10.0)

Fig. 16. Filter paper strips cultures of *Fusarium lactis* on Greathouse medium in which the ammonium nitrate has been replaced by an equivalent amount of ammonium phosphate and on Greathouse medium in which the ammonium nitrate has been replaced by an equivalent amount of ammonium sulfate. See p. 169.

Chaetomium globosum Kunze



NH_4NO_3 (pH 3.0–10.0)



NaNO_3 (pH 3.0–10.0)

Fig. 17. Filter paper strips cultures of *Chaetomium globosum*, Kunze at different pH and various nitrogen sources: Greathouse medium containing ammonium nitrate and on Greathouse medium in which the ammonium nitrate has been replaced by an equivalent amount of sodium nitrate. See p. 169.

Microbiodeterioration of Library Materials

Corda. The cultures were incubated at 24–26°C and 95% R.H. After 14 days the samples were picked out and washed with water to remove mycelium, and they were dried at ambient temperature. Tests to assess the mechanical properties of the samples were then carried out, and the decrease of strength was determined. It was established that only paper sheets damped with ethyl alcohol solution of 4-chloro-3-cresol were immunized.³ It is worth mentioning that papyrus may be preserved under glass, which is transparent and chemically inert in comparison to polystyrene, polymethylmethacrylate and polypropylene, which contain initiators, plasticizers, flame retarders and antioxidants that may lead to crazing and fine crack formation.⁷

4.3.2 Abstract

Decomposition of Papyrus by Microorganisms

From samples of papyrus different fungi and Actinomycetes were isolated. The genus *Chaetomium*, *Emericellopsis*, *Botryodiplodia* and *Streptomyces* play probably the greatest role in the decomposition of basic polymers of papyrus.

It was found that papyrus decomposing microorganisms may grow from 24 to 42°C and fungi loving low temperature occur rarely.

Out of four fungicides used, namely: Thymol, pentachlorophenol, dichlorophene and 4-chloro-3-cresol it was concluded that only 4-chloro-3-cresol may assure the protection of papyrus.

4.3.2 Résumé

Décomposition du papyrus par action microbienne.

Diverses moisissures et actinomycètes ont été isolés sur des échantillons de papyrus. Les espèces *Chaetomium*, *Emericellopsis*, *Botryodiplodia* et *Streptomyces* jouent probablement un rôle primordial dans la décomposition des polymères de base du papyrus.

Il a été prouvé que les microorganismes qui décomposent le papyrus peuvent croître dans une gamme de températures de 24 à 42°C et que les moisissures psychrophiles interviennent rarement.

Parmi les quatre rongicides utilisés, à savoir le thymol, le pentachlorophénol, le dichlorophène et le 4-chloro-3-crésol, seul le 4-chloro-3-crésol serait susceptible d'assurer la protection du papyrus.

4.3.2 Resümee

Zersetzung von Papyrus durch Mikroorganismen.

Aus Papyrus-Mustern wurden verschiedene Pilze und Strahlenpilze isoliert. Es ist anzunehmen, dass die Gattungen *Chaetomium*, *Emericellopsis*, *Botryodiplodia* und *Streptomyces* die grösste Rolle bei der Zersetzung der Hauptpolymere von Papyrus spielen.

Es wurde festgestellt, dass Mikroorganismen, die Papyrus zersetzen, bei Temperaturen von 24 bis 42°C ideale Wachstumsbedingungen haben, während Pilze, die niedrige Temperaturen vorziehen, selten auftreten.

Es wurde festgestellt, dass von den vier verwendeten Fungiziden, nämlich Thymol, Pentachlorophenol, Dichlorophenol und 4-Chlor-3-Kresol, lediglich ein, und zwar 4-Chlor-3-Kresol einen Schutz von Papyrus gewährleisten kann.



NH_4NO_3 (pH = 3.0–10.0)

NaNO_3 (pH = 3.0–10.0)

Fig. 15. Filter paper strips cultures of *Fusarium lactis*, Pirotta and Riboni on Greathouse medium containing ammonium nitrate and on Greathouse medium in which the ammonium nitrate has been replaced by an equivalent amount of sodium nitrate. See p. 169.

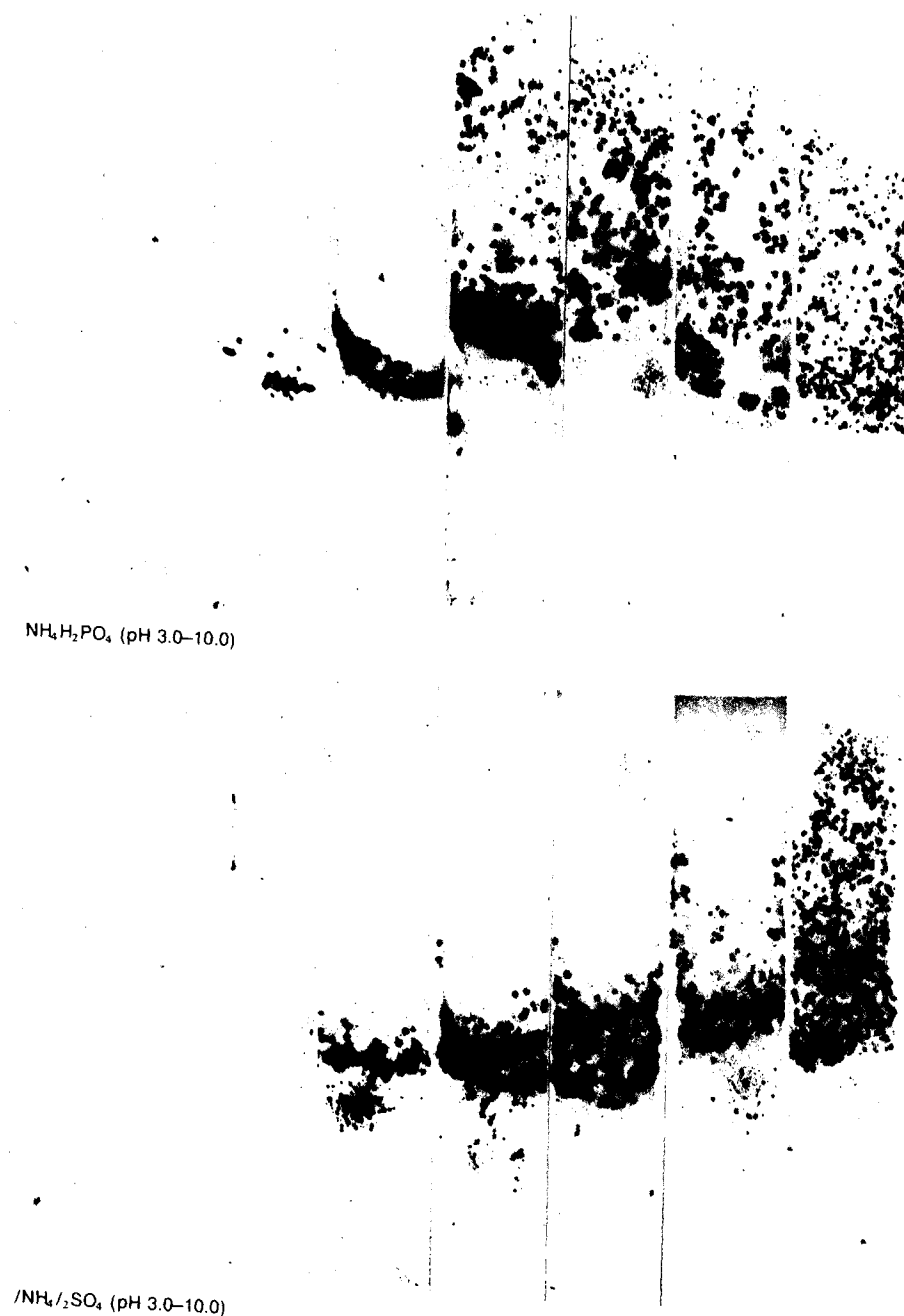


Fig. 18. Filter paper strips cultures of *Chaetomium globosum*, Kunze on Greathouse medium containing ammonium phosphate, and on Greathouse medium in which the ammonium phosphate has been replaced by an equivalent amount of ammonium sulfate. See p. 169.

4.3.3 References

1. Clapp, V. W., *The story of permanent durable book paper 1115–1970*. Restaurator, Supplement 3 (1972): 1–51.
2. Heppe, F. N. & Reynolds, T.: *Papyrus and the Adhesive Properties of its Cell Sap in Relation to Papermaking*. Journal of Egyptian Archaeology 53 (1967): 156–157.
3. Kowalik, R. & Sadurska, I.: *Microflora of Papyrus from Samples of Cairo Museums*. Studies in Conservation 18 (1973): 1–24.
4. Kowalik, R., Sadurska, I., Czerwińska, E.: *Microbiological Deterioration of Old Books and Manuscripts—Remedies*. Bolletino dell'Istituto di Patologia del Libro 21 (1962): 116–151.
5. Lucas, A. & Harris, J. R.: *Ancient Egyptian Materials and Industries*. E. Arnold Publishers Ltd., London 1962.
6. Plenderleith, H. J. & Werner, A. E. A.: *The Conservation of Antiquities and Works of ART*. London, New York, Toronto. Oxford University Press 1974.
7. Reed, R.: *Ancient Skins, Parchments and Leathers*. London, New York: Seminar Press 1972.
8. Smith, R. D.: *Treatment of Cellulosic Materials*. USPat. 3676182. July 11, 1972.

4.4.1 Decomposition of Paper by Microorganisms

When Arabia conquered Egypt, production of papyrus was continued, but in the tenth century it was completely replaced by paper.

In medieval periods paper was manufactured from careful selection of cotton rags and was not easily vulnerable to microorganisms. Afterwards the quality of paper violently changed for the worse. Certainly pH played a great role in the preservation of paper and in India rags were fermented with lime for several days. Of course raw material is also essential. Out of stern necessity paper was and is at present mostly produced from chemical wood pulp and it was observed that some books, newspapers and periodicals lost their strength by more than 50% within an estimated 10-year period of time and Cunha^{1, 8} estimates that in an average collection more damage has taken place during the five year span between 1970–1975 than occurred in the entire 18th century.

Poor quality modern papers, containing a great amount of polymers and nonfibrous material other than cellulose, and impurities, are especially conducive to prolific growth of microbial agents. There are however some specific microorganisms, for which cellulose is a source of carbon, the basic ingredient of food. This element is made accessible to them through the digestion of cellulose by the action of certain enzymes, which they can secrete.

In paper, the microorganisms have not only cellulose at their disposition, but also other substances such as lignin, hemicelluloses, pectins, waxes, tannins, proteins and mineral constituents. Furthermore, paper may contain resinous materials, fillers, dyestuffs, added during the productive cycle, and various

Microbiodegradation of Library Materials

impurities, for instance contaminating organic matter of human origin which may also form a part of the microbial diet.

Microorganisms influence the paper-making process from the time the tree is cut in the woods, or cotton or other natural products are harvested, until the finished product has completed its usefulness.³²

Paper may be subjected to the infection of different microorganisms during its production as when stored. The bacteria exist mainly in paper pulp since their development requires a high moisture content. On the other hand on finished paper, fungi and Actinomycetes occur the most often. They require a much lower moisture content and 100% R.H. may unadvantageously influence the development of some of them. Some species of common fungi are able to germinate at 70% R.H. or even lower (63–65%). These organisms vegetating on paper utilize intentional additives of adventitious impurities and prepare substrate for typical cellulolytic microorganisms. The abundance of microorganisms may occur after a flood. Omelianski,³⁸ after the flood of the River Neva in 1924, where 62,000 books were destroyed, isolated many fungi from the material of the Library of the Academy of Science of the USSR and advised the preservatives to protect books.

After the disastrous flood of November 4, 1966 in Tuscany, over thirty libraries and archives suffered extensive damage. Quite unexpected weather conditions also caused extensive flooding in December 1967 in Lisbon. Many valuable manuscripts on paper and parchment, belonging to the Calouste Gulbenkian collection were severely damaged.⁴¹ Other water-damage accidents in the USA are also well known as at the University of Corpus Christi Library 1971, Temple Law Library 1972, Federal Record Center, St. Louis 1972.⁹ Similarly serious deterioration was caused by the hurricane Agnes. As a consequence of tropical Agnes, June 1972, the flood of the Chemung River deposited a thick layer of mud on library and record archives, slide and film collections and devastated these materials at the Corning Museum of Glass,^{12, 14} where out of 13,000 volumes 6,500 were flood damaged.³¹ In Poland water damage accident appeared in the Jagiellonian Library in Cracow in 1980, where clean, white blotter papers impregnated with dichlorophene were interleaving in the drying process. Unusual deterioration of archives was caused by ice water rare in Quebec in 1975, where 75,000 volumes were damaged by microorganisms.⁴⁶

Such disasters involve the rapid movement of flood waters which carry with them materials derived from manifold activities of modern cities: chemicals, oils and different biological agents from sewage as bacteria, fungi, algae, which additionally develop rapidly after contact with the constituents of atmosphere.⁴¹

Paper may be destroyed by different species of microorganisms depending on its chemical composition, its acidity, its moisture content and the relative humidity of the environment, the temperature and light.

Polish old books and manuscripts suffered during the Second World War exceptionally severe deterioration owing to biological, physical and chemical causes. Samples of papers stored in different places of Poland were examined in order to have, if possible, a complete set of microorganisms which destroy old papers in our conditions. In the first place old papers from National Archives were tested. We took into consideration papers from the 15th century up to recent papers, samples of papers from graphic collections of Warsaw University, the National Museum in Warsaw, Cracow and Wrocław, Grottger collection and Caprichos of Goya from the Museum in Płock, papers from the Ministry of Foreign Affairs, records of the diocesan chancery in Wawel, former Nazi concentration camps of Oświęcim and Majdanek, and private collections.

Samples of papers which during the occupation or the period of vindication found themselves in various countries and in different environments yielded abundant amount of genera of fungi.

At first we examined pH of a sample of paper because a large complex of microorganisms is dependent on concentration of hydrogen ion. In acidic conditions at pH = 4.0 and less fungi are the only cellulolytic inhabitants of paper; bacteria need pH = 6.8–8.0. Actinomycetes grow best at pH = 5.0–8.0. At the greatest pH range however occurs fungi growth. Sometimes acidity changes may be used to prove the existence of microorganisms. pH was determined in our laboratory after extraction of paper with cold distilled water for two hours; in case of millboard and cardboard one day extraction was necessary. Papers having pH = 4.0–6.0 were more rapidly decomposed by microorganisms than papers having pH = 7.0 and more. Therefore for the production of durable paper more attention on pH should be paid.

Microorganisms were isolated by the following procedure: 80 × 80 mm samples of paper were cut out with a sterile tool from the centre of a sheet of paper (edges may happen to be contaminated). The samples of paper were washed with sterilized distilled water to eliminate surface contaminations and were then transferred to sterilized 100 mm diameter Petri dishes. In exceptional cases the method of impression to isolate the microorganisms from ancient valuable objects was used. Sterilized filter paper discs were pressed to mildew stains and then the discs were transferred to Petri dishes. With a sterile pipette 15 ml of liquid media were poured into every 100 Petri dish with paper sample of filter paper disc. We used the variety of elective media in order not to lose cellulolytic species. Besides papyrus, mentioned in section 4.3.1 some other cellulosic media were utilized: silica gel medium, medium from *Acetobacter*

xylinum membrane and agar with precipitated cellulose.³⁰ In order to obtain the optimal growth, fruiting or to identify the isolated species of fungi the following media: Sabouraud medium, brewers wort with gelatin or with agar, bean agar, potato-dextrose agar, dextrose agar, prune agar and others were utilized.^{29, 30}

After adding liquid media Petri dishes with a sheet of paper or with filter paper were kept under glass jars. Petri dishes were neither moved nor shaken during the whole experiment in order to avoid the contamination of growing cultures. The laboratory temperature of 18°C close to the temperature of libraries, archives or museums was quite satisfactory to incubate the cellulolytic microorganisms which probably cause staining of paper in natural conditions.

Samples of paper were not decomposed for a fairly long time since microorganisms utilizing cellulose as the only source of carbon are slow growing organisms.

After a period of several days, weeks or sometimes even months stains occurred on the surface of paper. Stains were composed of individual colonies or more often of a complex of microorganisms.

Paper destroying microorganisms were transferred with a fine sterile needle to a suitable culture medium. Individual species were purified and cultured on different media. In most cases Greathouse, Klemme and Barker medium with filter paper strips was used. It contains nitrogen source in two forms as nitrate and as ammonium ion. Several fungi however sporulated weakly on this medium and lost the ability to decompose cellulose. This could be to unsuitable balance of N:P; it is also possible that ammonium ion may inhibit the growth of some fungi because on a medium with nitrate as the only N source the fungi were well growing and fruiting.

During incubation many cases of growth stimulation of cellulose decomposing fungi were observed. Optimum of growth occurred in associated cultures which at the same time caused the decomposition of cellulose more intensely. Several purified cultures were unable to grow on synthetic media without the nourishment which the associated organism was preparing. The greatest growth stimulation appeared at organisms as taxonomically remote as *Chaetomium* genus and bacteria; *Trichoderma viride*, *Streptomyces cellulosa* and *Rhodotorula mucilaginosa*.

To examine the stages of fungi growth and spore production small squares 1.5 × 1.5 cm from transparent viscose film were used. On a wad imbibed with liquid, diluted 1:10 Greathouse, Klemme and Barker medium or other medium specific for a given species, about ten small squares of film in a Petri dish were laid. After sterilization at 1 atmosphere and cooling every square of film was inoculated at one or more points. Single pieces of film were removed at 24-hour

intervals for examination and taking photographs. To take various stages of fungi, Kino-Exacta apparatus and 17°DIN cartridge Isopan F were used and Leitz microscope, as also Reichert microscope with camera.

To demonstrate coloured stains and destructions made by microorganisms on the surface of potato dextrose agar medium circles of paper inoculated at its centre with the spores or fungal hyphae were laid. After a colony was grown sufficiently the circles of paper were lifted out of the dish and sterilized with 5% formaldehyde vapours for the preparation of museum specimens of mould colonies.

With the help of these methods the following fungi were isolated^{29, 30}:

From class Basidiomyceteae, order Polyporales, family Thelephoraceae *Pellicularia isabellina*, (Fr) Rogers (Fig. 1).

From order Agaricales, family Agaricaceae *Coprinus* sp., (Pers. ex Fr.) Fray probably sclerotinogenus.

Many species of genus *Chaetomium* (Figs. 2–15) were isolated from class Ascomyceteae, order Sphaeriales, family Chaetomiaceae. It was observed that members of this genus break down papers of poor quality and rarely disintegrate rag-made papers.

Pestalotia sp., de Notaris was isolated from 17th and 18th century papers. It developed black stains on paper and a light rose zone around the spot.

From order Sphaeropsidales, family Sphaeropsidaceae *Phoma humicola*, Gilman and Abbott, was isolated. On the paper grey-brown or black spots were observed.

From records of Ministry of Foreign Affairs *Chaetomella horrida*, Oudemans giving grey-brown spots was isolated (Fig. 16).

From order Moniliales *Cephalosporium acremonium*, Corda the most often paper-loving microorganism was observed. This fungus was staining paper from orange to rose tints according to pH.

Trichoderma viride, Pers. ex. Fr. (Figs. 17, 18) was found most often on regenerated cellulose, but paper's cellulose was also destroyed in 40% in 20 days. It developed on paper dark green coloured colonies and stained it light green.

From *Aspergilli* (Figs. 19–26) a dozen or so species were isolated from paper and *Aspergillus fumigatus*, Fresenius, played an important part in the deterioration of paper. The most active strains developed at the beginning grey, afterwards green and at last dull brown colour on paper.

Aspergillus Wentii, Wehmer, destroyed paper rather slightly and coloured it light rose. *Aspergillus niger*, van Tieghem, appeared often on paper and in presence of glucose decreased cellulosic material resistance considerably. On paper minute black superficial colonies were observed.

From genus *Penicillium* some species or strains were isolated (Figs. 27, 28).

Old paper did not offer a satisfactory medium for *Penicillia* and *Aspergilli*, but these species which need only 7–9% of moisture contained in paper to grow, moistured the paper and due to this fact enabled contamination and growth of more active cellulolytic fungi.

Assigned to *Penicillium* group *Paecilomyces varioti*, Bainier (Fig. 29) injured paper slightly and its colonies developed light yellow-brownish shades. *Spicaria* gave Lilac spots (Fig. 31).

Scopulariopsis brevicaulis (Sacc.) Bainier, like *Paecilomyces* related to *Penicillium* injured paper distinctly and willingly utilized ammonium ion as N source (Fig. 30).

Botryotrichum atrogriseum van Beyma decomposed paper strongly. Spots on the paper caused by this species developed steel-grey shades. It occurred abundantly on papers from the 16th and 17th centuries.

More rarely appeared on paper *Sepedonium* Link which formed white-grey growth and spots on paper.

Botrytis cinerea Persoon (Fig. 32) grew on paper in the form of delicate colonies and grew well to 2 mm above the surface of the paper. It formed mycelial sclerotia of several mm diameter. The best N source for *Botrytis* was ammonium sulphate at pH = 8.0, but the growth occurred even at pH = 3.0. Apart from ammonium sulphate other N salts, as ammonium nitrate, sodium nitrate, ammonium phosphate, pepton and asparagin were utilized. From C source it utilized at higher concentration 0.5–1% saccharose, mannose, maltose, glucose, galactose, xylose and glycerol. At lower concentration it sporulated poorly and lower concentration of glycerol did not support the growth.

Acrostalagmus cinnabarinus, Corda (Figs. 33, 34) stained paper to rusty shades.

Eidamella spinosa, Matrucho and Dassonville (Fig. 35) developed amaranthine great spots and injured cellulose strongly. Therefore this species should be considered dangerous for paper stocks.

From family *Dematiaceae* *Mycogone nigra* (Morgan) Jensen (Fig. 35a) was isolated. It decomposed cellulose intensely and developed dark-green spots on paper. It grew in wide temperature range from 5–30°C, optimum temperature being 20–25°C. Well utilized different N sources and some C sources.^{29, 30}

Torula, Persoon (Fig. 36) caused black spots on paper. *Stachybotrys atra*, Corda (Fig. 37) stained and covered paper with black or greenish-black growth with greenish-grey or brown zones. This species was isolated several times from paper of the 16th to 20th centuries.

Gliomastix convoluta, (Marchal) Mason stained paper black and decomposed it strongly and *Gliocladium roseum* (Link) Thom (Fig. 38) stained paper rose.

Trichocladium, Harz (Fig. 39) injured paper strongly and stained it greenish-yellow or greenish-rusty depending on strains and pH.

Cladosporium herbarum (Persoon) Link (Fig. 40) occurred on various papers. This species was resistant both at low and high temperatures and grew at different pH concentration and high fungicide concentration.

Helminthosporium, Link (Fig. 41) stained paper greyish-white. It grew and sporulated best on regenerated cellulose.

Curvularia lunata (Walker) Boedijn (Figs. 42, 43) covered paper by black spots and afterwards developed larger spots. This species decomposed paper severely. The best N source for this fungus was ammonium phosphate.

Trichothecium roseum, Link (Fig. 44) developed on paper fluffy colonies growing well; they formed at the beginning white, afterwards pale-rose stains. The best N source for this species was ammonium phosphate.

Acrothecium, Preuss strongly decomposed paper staining it olive-green. The best N source for it was urea. (Fig. 45).

The representatives of *Alternaria* (Figs. 46, 47) genus occurred often on different sorts of paper, as also *Stemphylium* (Fig. 48) genus. They developed black, dark-brown and brown-greenish spots. They deteriorated paper intensely.

Family *Tuberculariaceae* was in our experiments represented by *Epicoccum nigrum*, Link. This species developed on paper black colonies adhering tightly to the fibres. The best N source for this fungus was ammonium phosphate at pH = 7.0. This species degenerated rapidly in artificial cultures in our laboratory. Treatment of its colonies or spores with ultrasonics in piezoelectric generator at 1 MHz frequency of vibration and at 120 mA anodic current density during a period of 2 minutes stimulated the sporulation of this fungus. Treating it with ultrasonics also caused changes in N source utilization and sporodochia (fruiting bodies) development. Sodium nitrate at pH = 4.0 and urea at pH = 6.0 was best utilized by the strain treated with ultrasonics.

Many species of *Fusarium* genus were isolated from paper (Figs. 49, 50, 51). They discoloured paper giving violet tints, blue spots, pink-violet spots and yellowish-pink tints.

From the family *Actinomycetaceae* many paper-loving organisms were isolated. They produced on paper a variety of colours: powder-pink, yellow, grey and black, white. They strongly decomposed cellulose, depending on pH and N sources (Figs. 52, 53).

At a high relative humidity 80–90% and high moisture content in paper several bacteria: *Cellfalcicula*, *Cellvibrio* and *Cytophaga* were isolated. They intensely discoloured paper.

The most often observed paper-destroying organisms were the following: *Stachybotrys*, *Chaetomium*, *Cladosporium*, after *Alternaria*, *Stemphylium*, *Trichoderma*, *Botryotrichum*, *Aspergillus fumigatus*, *Eidamella spinosa*, *Sepedonium*, *Mycogone*, *Penicillium* from luteum group, *Cephalosporium* often occurred on paper. *Trichocladium*,



Fig. 1. *Pellicularia isabellina*, (Fr.) Rogers. ($\times 420$).



Fig. 2. *Chaetomium bostrychodes*, Zopf. ($\times 250$).

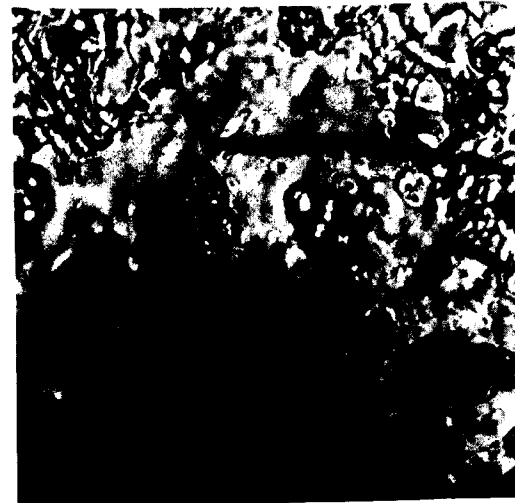


Fig. 7. *Chaetomium globosum*, Kunze: Spores in asci. ($\times 500$).



Fig. 8. *Chaetomium fusiforme*, Chivers. ($\times 250$).



Fig. 3. *Chaetomium bostrychodes*, Zopf. ($\times 420$).



Fig. 4. *Chaetomium cochliodes*, Palliser. ($\times 500$).



Fig. 9. *Chaetomium* probably *turgidopilosum*, Ames. ($\times 250$).



Fig. 10. *Chaetomium* probably *atrobrunneum*, Ames. ($\times 250$).



Fig. 5. *Chaetomium contortum*, Peck. ($\times 100$).



Fig. 6. *Chaetomium aterrimum*, Ellis and Everhart. ($\times 100$).



Fig. 11. *Chaetomium ochraceum*, Tschudy. ($\times 250$).



Fig. 12. *Chaetomium olivaceum*, Cook and Ellis. ($\times 100$).

Chaetomium cochlioides Palliser

$\text{NH}_4\text{H}_2\text{PO}_4$ (pH = 3.0–10.0)

$/\text{NH}_4/2\text{SO}_4$ (pH = 3.0–10.0)

Fig. 15.



Fig. 21. *Aspergillus flavus*, Link. (× 500).



Fig. 22. *Aspergillus niger*, van Tieghem. (× 420).



Fig. 23. *Aspergillus niger*, van Tieghem. (× 420).

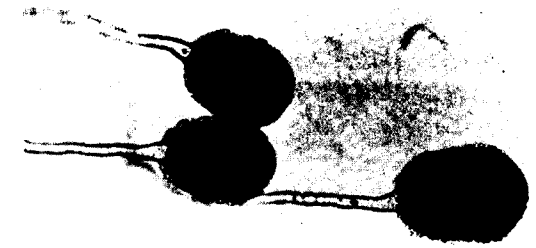


Fig. 24. *Aspergillus terreus*, Thom. (× 250).



Fig. 25. *Aspergillus terreus*, Thom. (× 500).

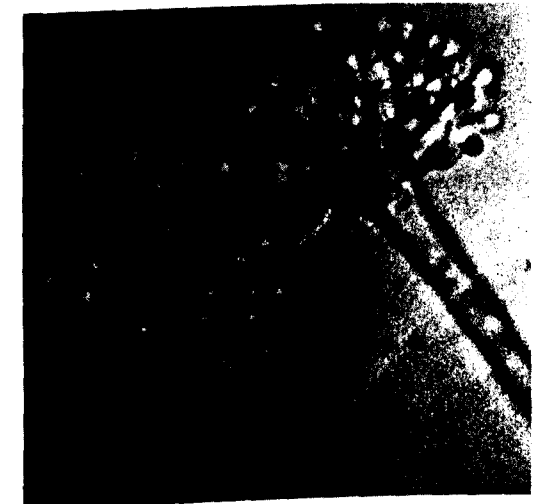


Fig. 26. *Aspergillus* sp. (× 500).

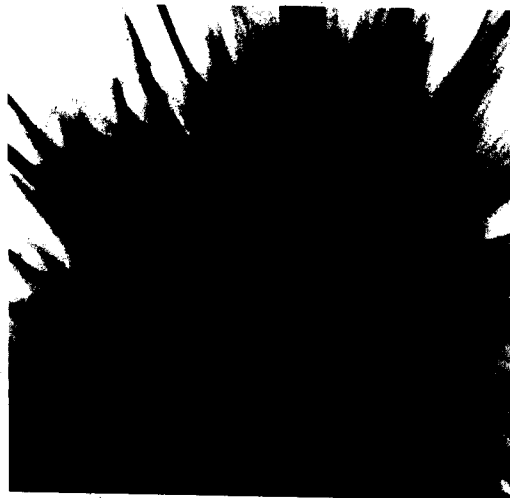


Fig. 13. *Chaetomium angustum*, Chivers. ($\times 250$).



Fig. 16. *Chaetomella horrida*, Oudemans. ($\times 250$).

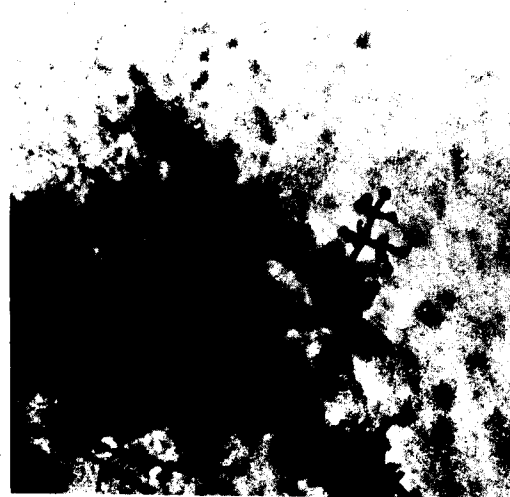


Fig. 17. *Trichoderma viride*, Persoon ex Fries. ($\times 250$).



Fig. 18. *Trichoderma viride*, Persoon ex Fries. ($\times 500$).



Fig. 19. *Aspergillus amstelodami*, (Mangin) Thom. ($\times 420$).

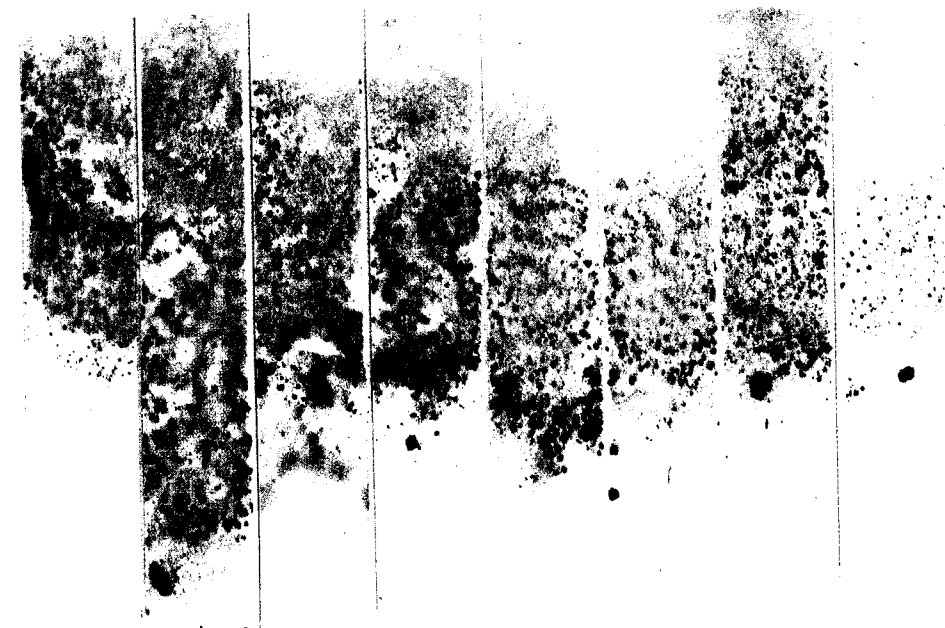


Fig. 20. *Aspergillus candidus*, Link. ($\times 420$).

Chaetomium cochlioides Palliser



NH_4NO_3 (pH = 3.0–10.0)



NaNO_3 (pH = 3.0–10.0)

Fig. 14.

Fig. 14 and 15. *Chaetomium cochlioides*, Palliser cultivated on filter paper strips at different pH and different N sources. See p. 175.



Fig. 27. *Penicillium brevi-compactum*, Dierck. (× 250).

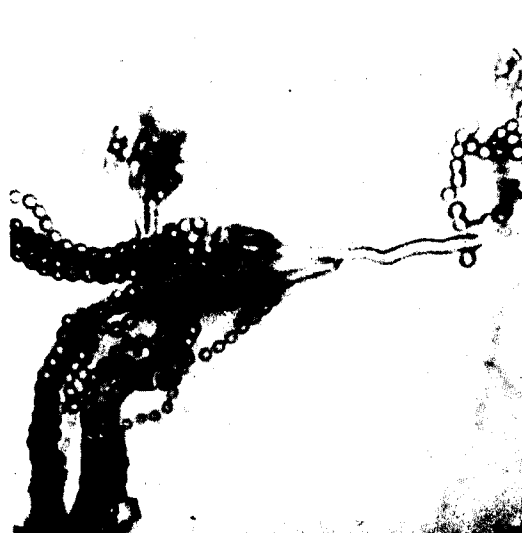


Fig. 28. *Penicillium* sp. (× 500).



Fig. 29. *Paecilomyces varioti*, Bainier. (× 250).



Fig. 30. *Scopulariopsis brevicaulis*, Bainier. (× 250).



Fig. 31. *Spicaria violacea*, Abbott. (× 500).



Fig. 32. *Botrytis cinerea*, Persoon. (× 250).



Fig. 33. *Acrostalagmus cinnabarinus*, Corda var. *nana* Oudemans. (× 150).

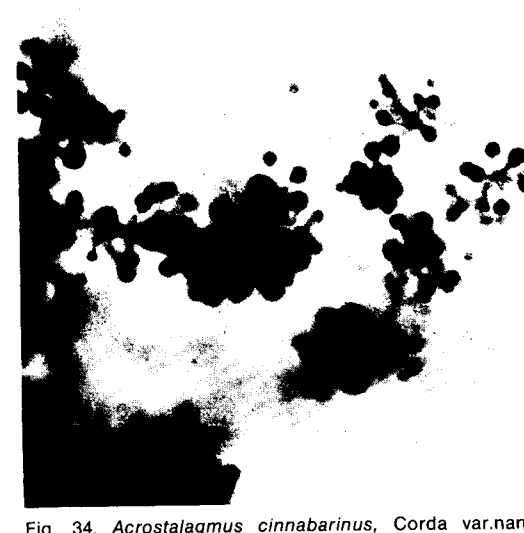


Fig. 34. *Acrostalagmus cinnabarinus*, Corda var. *nana* Oudemans. (× 420).



Fig. 35. *Eidamella spinosa*, Matruchot and Dassonville. (× 420).

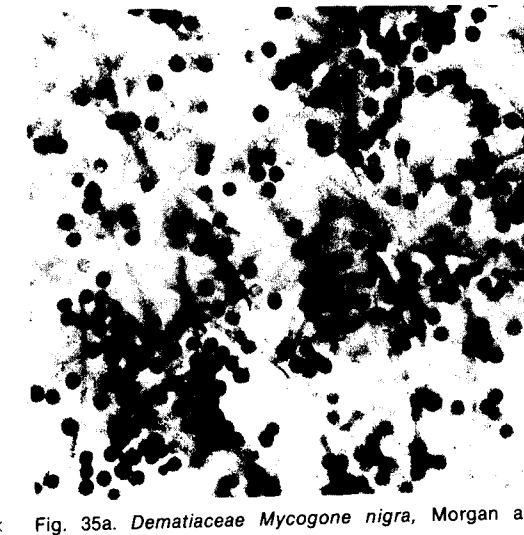


Fig. 35a. *Dematiaceae Mycogone nigra*, Morgan and Jensen.

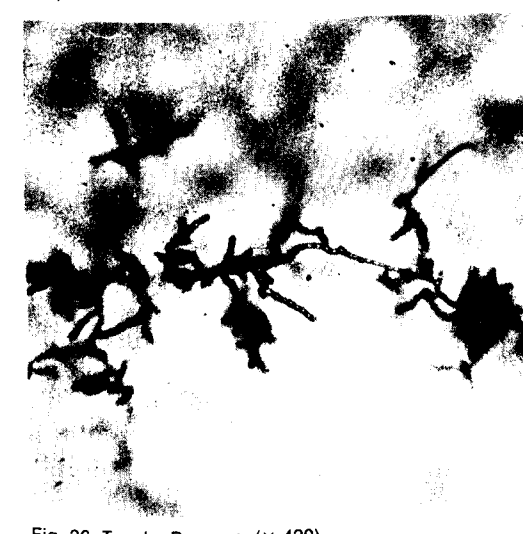


Fig. 36. *Torula*, Persoon. (× 420).

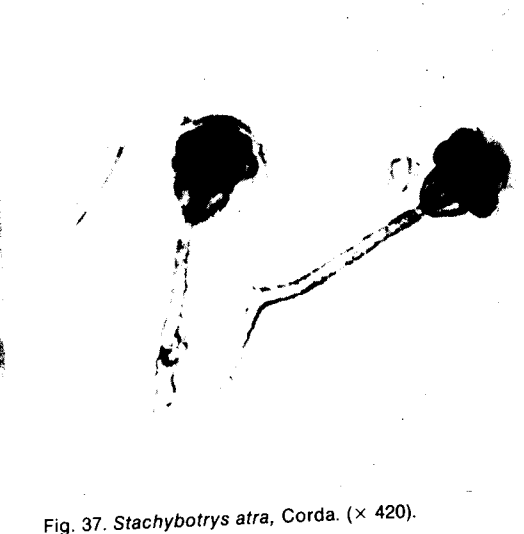


Fig. 37. *Stachybotrys atra*, Corda. (× 420).



Fig. 38. *Gliocladium roseum*, (Link) Thom. ($\times 250$).



Fig. 39. *Trichocladium*, Harz. ($\times 420$).



Fig. 44. *Trichothecium roseum*, Link. ($\times 250$).



Fig. 45. *Acrothecium*, Preuss. ($\times 250$).



Fig. 40. *Cladosporium herbarum*, (Persoon) Link. ($\times 500$).



Fig. 41. *Helminthosporium*, Link. ($\times 250$).



Fig. 46. *Alternaria tenuis*, Nees. ($\times 250$).

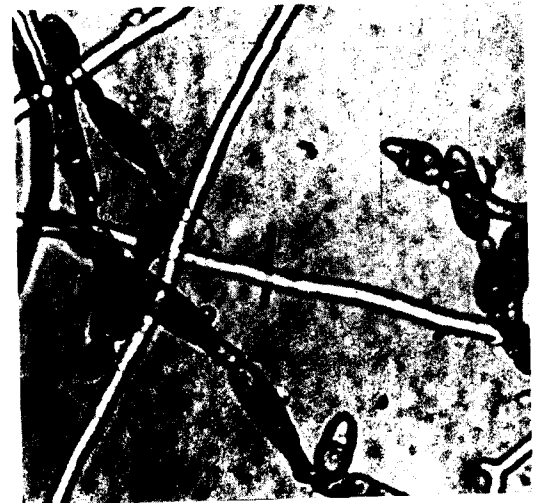


Fig. 47. *Alternaria* sp. ($\times 500$).



Fig. 42. *Curvularia lunata*, (Walker) Boedijn. ($\times 250$).



Fig. 43. *Curvularia lunata*, (Walker) Boedijn. ($\times 420$).



Fig. 48. *Stemphylium lanuginosum*, Harz. ($\times 250$).



Fig. 49. *Fusarium* probably *anguoides*, Sherbakoff. ($\times 250$).

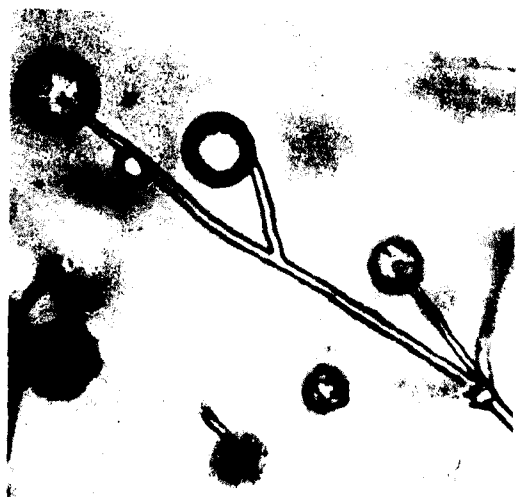


Fig. 50. *Fusarium oxysporum*, Schlechtendahl. ($\times 500$).



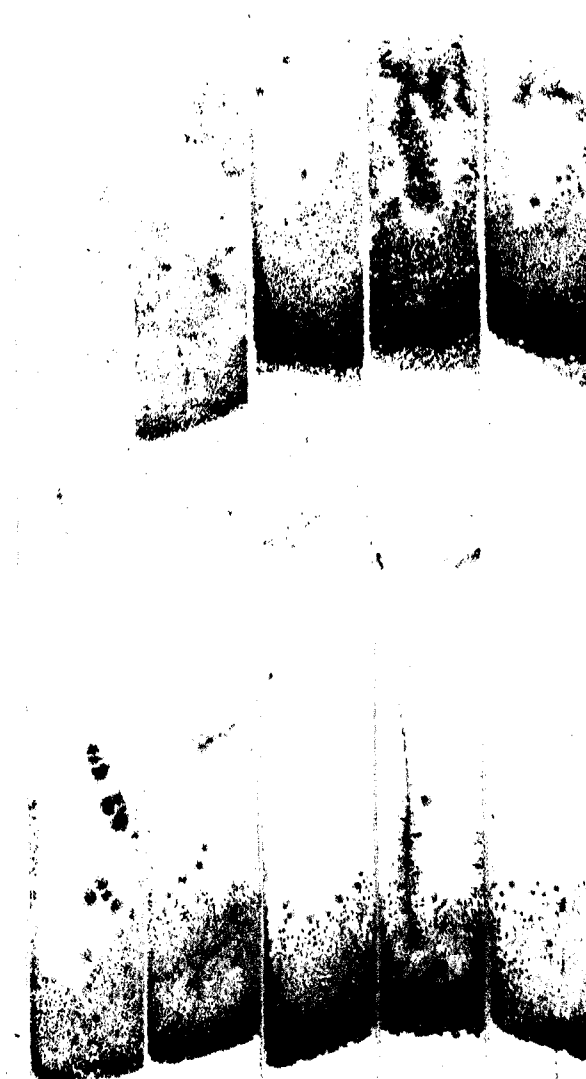
Fig. 51. *Fusarium* probably *sambucinum*, Fuckel. ($\times 250$).

Torula, *Botrytis*, *Pellicularia* were rarely observed. *Scopulariopsis*, *Epicoccum*, *Curvularia*, *Trichothecium* and a few strains of *Fusarium*, *Gliomastix*, *Aspergillus niger*, *Pestalotia*, *Acrothecium*, *Paecilomyces* were observed several times as well as many unidentified species probably belonging to *Basidiomycetes*.

As for a preservation of microorganisms isolated from paper is concerned sterilized neutral paraffin oil was from our point of view the most convenient. By using this method the activity and vitality of our collection of different material-deteriorating microorganisms was maintained for 20 years.

For the preservation of paper against microorganisms after isolation of microbial agents, which hydrolyse cellulose and other components of paper the purpose of the next step of our work was the suggestion of suitable microbiotoxicant, appropriate method of addition and the correct quantity, required to stop metabolic processes of the microorganisms or to protect the cellulose object against microbial activity. One of the ways to prevent the growth of microflora is to make use of bacteri- and fungitoxicants (Tab. 1), which may act immediately or prophylactically.

The application of preventive techniques to paper supposes the general consideration of the influence of biocide on paper, the conditions in which they will be used, and the study of the activity of these compounds on a particular group of microorganisms. It is important to understand the physical and physico-chemical properties of the fungicides themselves, the ease and uniformity of their deposition on the paper and the time during which the protection can be



NH_4NO_3 (pH = 3.0–10.0)

NaNO_3 (pH = 3.0–10.0)

Fig. 52. Filter paper strip cultures of *Streptomyces melanocyclus*. (Merker) Waksman and Henrici at different pH and various nitrogen sources (NH_4NO_3 and NaNO_3). See p. 177.

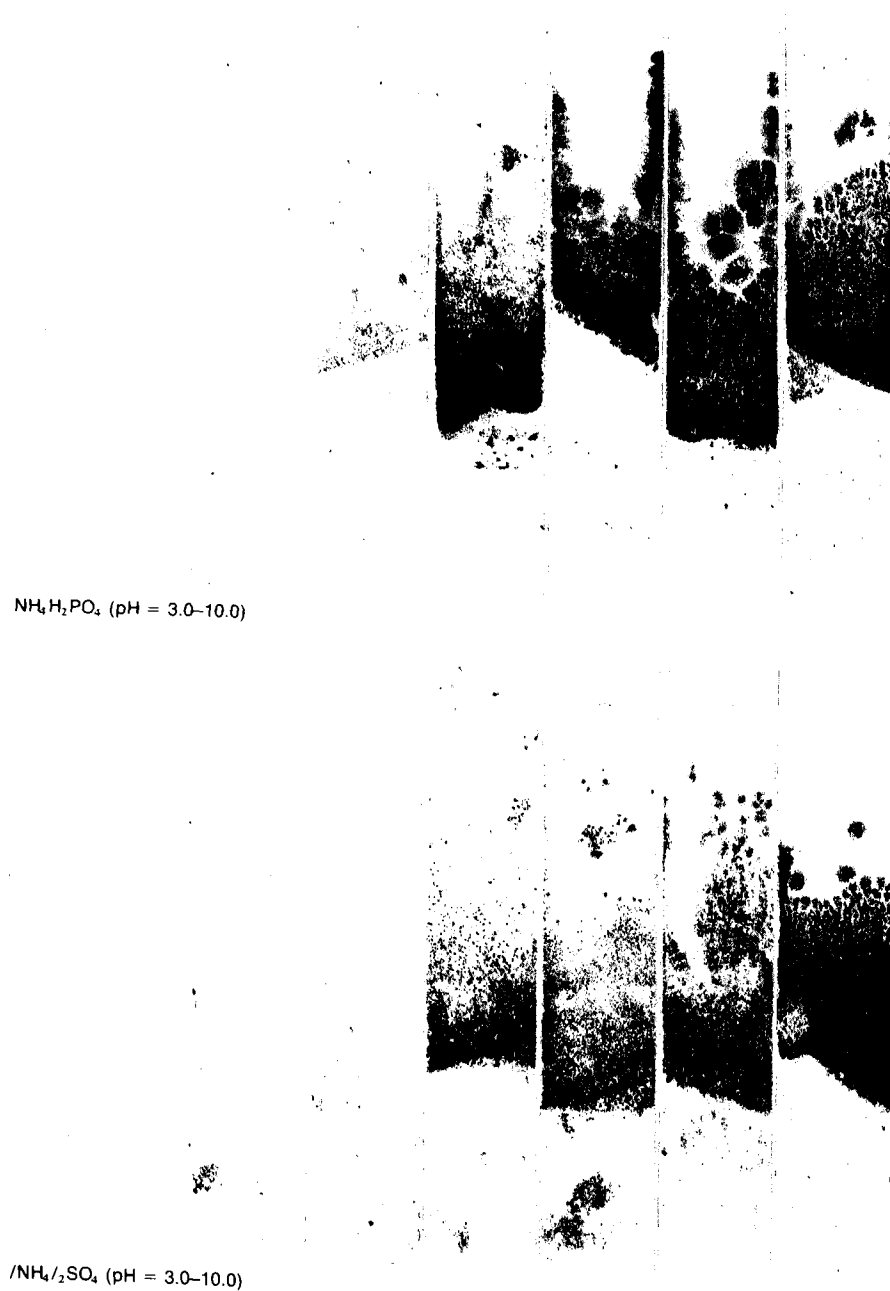


Fig. 53. Filter paper strip cultures of *Streptomyces melanocyclus*, (Merker) Waksman and Henrici at different pH and various nitrogen sources ($\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{NH}_4/2\text{SO}_4$). See p. 177.

guaranteed. They should be easy to apply and they should satisfy the criteria of low toxicity to man and to the environment. Numerous fungi- and bactericides proposed for the protection of paper were evaluated in our laboratory, including recently tested 2,4,4'-trichloro-2'-dihydroxydiphenylether (Irgasan DP-30) in comparison to 2,2'-dihydroxy-5,5'-dichlorodiphenylmethane (dichlorophene). Although Irgasan DP-300 was in vitro less active than dichlorophene against: *Alternaria tenuis*, *Aspergillus terreus*, *Aspergillus niger*, *Chaetomium globosum*, *Fusarium solani*, *Paecilomyces varioti*, *Penicillium funiculosum*, *Stachybotrys atra*, *Trichoderma viride*, fabric however treated with 1% ethanol solution of Irgasan DP-300 similarly to dichlorophene protected effectively against soil microorganisms in soil burial tests.

Because thymol in convenient vapour form was and is often used by conservators,^{17, 33, 54} I relate our own tests. Thymol was investigated in our laboratory on fungi decomposing old paper: *Aspergillus niger*, van Tieghem, *Chaetomium globosum*, Kunze, *Epicoccum purpurascens*, Ehrenberg, *Penicillium vermiculatum*, Dangeard, *Stachybotrys atra*, Corda, *Streptomyces cellulosae*, Krainsky. Crystal of thymol (melting point of thymol is 51.5°C) were placed on the bottom of the desiccator and the sheet of cardboard on the porcelain insertion.

To generate the vapours the bottom of the desiccator was heated to the temperature of 52°C every day for 2 hours for 14 days. Cardboard was held in these conditions the whole time, every day 70 g/m³ of thymol was added. As was found by control some fungi existed in the cardboard but these did not grow anymore already after 6 days of thymol fumigation. On the contrary, on a cardboard inoculated with fresh good sporulating cultures of fungi even after 14 days of treatment with thymol vapours growth occurred. Fungi existing in cardboard were probably weakened owing to lack of water and were therefore easier to kill than fresh well fruiting fungi. According to Werner⁵⁵ thymol has some disadvantages. It can act as a very powerful solvent, sometimes with devastating results.

Recently we have tested the vapour fungitoxic action of p-dichlorobenzene (Fig. 54). This compound is known as insecticide. The books infected should be placed in the container and exposed to the vapours but not allowed to touch the crystals. According to Block^{3, 4} and others^{27, 34, 49} p-dichlorobenzene is also effective in inhibiting the fungal growth in closed spaces. p-Dichlorobenzene has been also effective against fungi in shoes, cotton, wool samples and books contaminated with *Aspergillus niger*, *Aspergillus ustus*, *Penicillium sp.*, *Chaetomium globosum*, *Myrothecium verrucaria*.⁴⁴ It seemed interesting to us to examine p-dichlorobenzene on several typical book-deteriorating fungi. We have found that p-dichlorobenzene at the amount of 50 g/m³ inhibits completely the growth of *Chaetomium globosum*, Kunze, *Stachybotrys atra*, Corda, *Trichoderma viride*,

Table 1. The more important fungi- and bactericides proposed to protect library materials.
 Tableau 1. Les fongicides et les bactéricides les plus importants proposés pour la protection des matériels de librairie.
 Tabelle 1. Die wichtigsten Fungizide und Bakterizide, die zum Schutz von Büchereibeständen empfohlen werden.

Structural formula	Chemical name	Trade name	Field of application	Melting point	Colour	Solubility	Toxicity	Remarks
ORGANIC COMPOUNDS								
1	2	3	4	5	6	7	8	9
	1,2-epoxyethane	Ethylene oxide, Carboxide	different materials	107°C	colourless liquid	Miscible with water and organic solvents	Concentrations above 3000 ppm dangerous if inhaled for 30 minutes or more	
	p-dichlorobenzene	Paracide, PDB	Commonly used to protect fabrics and clothing	53°C	crystals white	very slightly soluble in water and alcohol, soluble in most organic solvents	LD ₅₀ to rats p.o. 2,56g/kg. Fumes irritant for eyes	fumigant fungistatic
	o-phenylphenol	Preventol O, Dowicide A	cellulosics, wax, seals, inks	57°C	colourless	in most organic solvents	LD ₅₀ to rats 2,48g/kg	sodium salt soluble in water, acetone, alcohol, insoluble in petrol oil
	2,2'-dihydroxy-5,5'-dichlorodiphenylmethane	Dichlorophene, Preventol GD, G4, DDM, DDD M	cellulosics, glues, paints, varnishes	177-178°C	pure compound colourless, commercial compound tan coloured	slightly soluble in ethyl alcohol, acetone	LD ₅₀ to dogs 2g/kg p.o.	alkali salt soluble in water
	2,2'-dihydroxy-5,5'-dichlorodiphenylsulfide	Fentichlor	collagenics		colourless	in water, 76% in ethanol	low toxicity	broad spectrum of activity in a great pH range
	4-chloro-3-cresol, 6-chloro-3-oxy-methylbenzene	Raschit, Preventol CMK	cellulosics, glue, leather, paint, parchment	66°C	colourless	in most organic solvents	skin irritating	sodium salt soluble in water
	isopropyl cresol	Thymol	cellulosics, (parchment)	49-51°C	colourless	ethyl alcohol, carbon sulphide, glacial acetic acid, ethyl ether, oils, slightly soluble in water, glycerol	probable LD to humans 50-500 mg/kg p.o. skin irritant in concentration higher than 2%	
	2,4,6-trichlorophenol	Dowicide 2S	cellulosics	69°C	colourless	in most organic solvents	LD ₅₀ to rats 820 mg/kg p.o.	sodium salt freely soluble in water
	pentachlorophenol	PCP, penta	cellulosics	191°C	tan coloured	in most organic solvents	LD ₅₀ to rats 210 mg/kg p.o. skin irritant easily absorbed by skin from air, food, water	sodium salt water-soluble, giv- es in the light a red product

	lauryl penta-chlorophenol	Mystox, LPL, LSL	cellulosics, plastics, paints		colourless	benzene, acetone, oil, waxes, plasticizers		
	n-phenyl salicylamide	Shirilan	cellulosics, leather, paints	135°C	cream coloured	in most organic solvents	low toxicity LD ₅₀ to rats higher than 2000 mg/kg p.o.	
	3,5,3',4'-tetrachlorosalicylamide	Irgasan BS-200	cellulosics, plastics	161-169°C	white	in most organic solvents	low toxicity	
	zinc dimethyldithiocarbamate	Ziram (common name)	cellulosics, plastics	240°C	white	soluble in carbon disulphide, dilute alkalies, strong ammonia solution	low toxicity LD ₅₀ to rats 1400-1500 mg/kg p.o. recognized carcinogen	
	Zinc naphthenate		textiles	148-152°C	light blue green coloured	soluble in most organic solvents	low toxicity	
	Copper 8-hydroxyquinolate	Acryptol Cu, Preventol C ₉	textiles	does not melt	yellow coloured	common organic solvents	low toxicity LD to man 5-15g/kg	
	phenylmercurioacetate	PMA, PMAc, PMAS	cellulosics, paints	149-153°C	colourless	ethyl alcohol, acetone, benzene	highly toxic	
	bis(tri-n-butyl-tin) oxide	TBTO	cellulosics, paints	180°C	colourless	miscible with most organic solvents	LD ₅₀ to rats 148 mg/kg p.o. may be absorbed by skin	
	2,4,4'-trichloro-2'-hydroxydiphenylether	Irgasan DP-300	cellulosics	54-57°C	colourless	in most organic solvents	LD ₅₀ to rats 29 g/kg p.o.	fungi-ana-bactericide
	lauryl dimethylbenzyl ammonium chloride	Zephiran Sterinol	different materials, disinfecting agent		colourless	in water	LD ₅₀ to rats 300 mg/kg p.o.	bacteriostatic

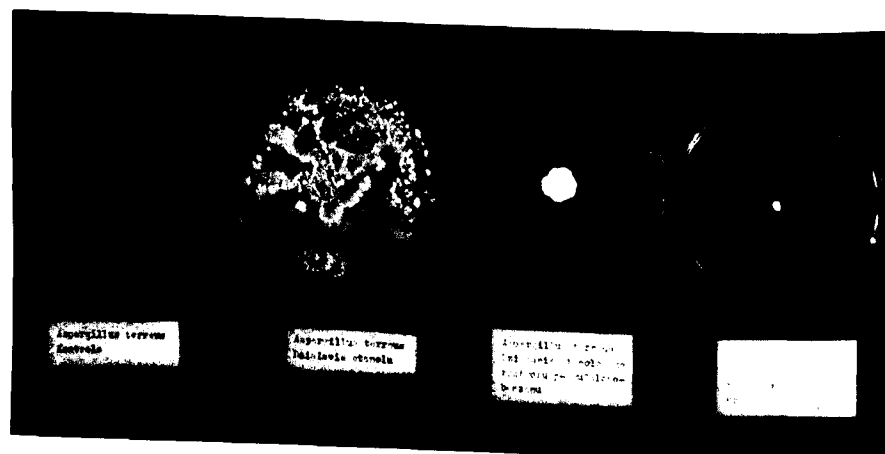
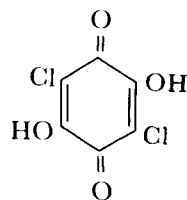


Fig. 54. The comparison of fungitoxic activity of p-dichlorobenzene and 4-chloro-3-cresol: a) Control, b) The activity of ethanol, c) the activity of ethanol solution of p-dichlorobenzene at the concentration of 10 g/m³, d) the activity of ethanol solution of 4-chloro-3-cresol at the concentration of 10 g/m³, on *Aspergillus terreus* Thom.

Persoon, but is fungistatic only against *Aspergillus flavus*, Link, *Aspergillus terreus*, Thom and *Penicillium funiculosum*, Thom (Fig. 54).

For old papers and documents destined for permanent preservation a mixture of thymol and mercuric chloride in ether-benzene solution,¹⁷ the sodium salt of dichlorophene,^{26, 27} lauryldimethylcarboxymethyl ammonium bromide,^{cit. 27} sodium salt of pentachlorophenol^{2, 20, 40} in water and also salicylanilide in trichloroethylene and acetone solution³⁷ have been used in effectiveness. Salicylanilide is effective in the case of paper having a low moisture content, but it is not maintained for long in the fibre when subjected to a continual humidity.³ The mixture of mercuric chloride and thymol is strongly toxic and increases a little the acidity of paper.²⁶ Pentachlorophenol, besides being toxic, is weakly acidic and gives in light besides hydrochloride, a red product chloranilic acid



and other coloured components.³⁶ Quarternary ammonium compounds are effective only against G positive bacteria and they could be used rather together



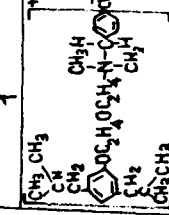
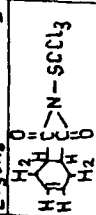
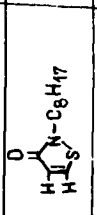
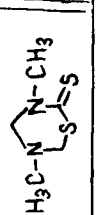
Fig. 55. The sample of petrified book under the influence of among others, microbial agents.

with o-phenolphenol. According to Zappala⁵⁶ lauryl dimethyl carbatoxy methyl ammonium bromide (Cequartyl BE) has been shown not to be chemically inert and is deleterious towards the cellulose. Hyamine 1622, produced by Rohm and Haas, tested by us is effective against fungi and bacteria but it is not sufficient to utilize it for paper.

Dichlorophene seems to be suitable for unwritten paper and for blotting paper impregnated with it and used for insertion between the damp leaves of books. It does not change the pH. Dichlorophene may be harmful when applied immediately to the documents written with ink. Moreover, as other chlorinated phenols it is somewhat volatile and presents a potential danger on release of chlorine on decomposition. Ester di-MCA is a better protectant than dichlorophene itself and did not colour the cellulose materials, but monoester of monochloroacetic acid and 2,2'-methylenebis (4-chlorophenol) discoloured cellulosic materials as badly as original bisphenol.^{18, 19}

For the immediate killing of microorganisms, but not immunizing the object, ethylene oxide seems to be the most suitable.²⁸ When 90% carbon dioxide is present or about the same percentage of various fluorinated hydrocarbons (CCl₂F₂ and CCl₃F) the resulting mixture can in turn be mixed with air in all proportions without passing through an inflammable state.^{28, 34, 48} In this last

Table 1. Continued.

Structural formula	Chemical name	Trade name	Field of application	Melting point	Colour	Solubility	Toxicity	Remarks
ORGANIC COMPOUNDS								
1	2	3	4	5	6	7	8	9
	disobutylphenoxy-ethoxy-ethyl dimethylbenzyl ammonium chloride	Hyamine 1622	cellulosics with emulsion		colourless	in water	low toxicity	
	N-(4-chlorophenyl)-N-(4-ethoxyphenyl)ethanimmonium chloride	Captan	plastics, paints	178°C	white	partly in acetone, benzene, toluene, xylene, chloroform	LD ₅₀ to rats 5000 mg/kg p.a., may cause skin irritation	
	actyl-4-izothiazola-3-one	Kathon LP	collagenics		colourless	in water	LD ₅₀ to rats 3180 mg/kg p.a.	against fungi and bacteria G+ and G-
	dimethyl-tetrahydrothiadiazin	Dazomet, DMF, CosanS	collagenics			in water	low toxicity	broad spectrum from 20-2000 ppm at the pH from 4.0-9.0
INORGANIC COMPOUNDS								
H_3BO_3	boric acid		stone, leather, adhesives, wood	184°C		in water	LD to man 15-20g/kg	
$Na_4B_4O_7 \cdot H_3BO_3$	borax + boric acid	Polybor	stone, wood	borax 75°C		in water, ethanol	LD to man 0.5-15g/kg	
$SU_2Cu(NH_3)_4$	tetramine copper sulphate		stone				low toxicity	
$NaClO_2$	sodium chloride		paper					fire and explosion hazard
INORGANIC COMPOUNDS								
$ZnCl_2$	zinc chloride		wood, textiles	290°C			LD ₅₀ for mice 31mg/kg, human inhalation of 4800 mg/m ³ for 1/2 hour pulmonary effects. The fumes highly toxic	
NaF	sodium fluoride		wood	993°C	clear white	in water 4.3%	LD ₅₀ for rat 180 mg/kg	
$(NH_4)_2F_2$	ammonium fluoride		wood			in water	LD ₅₀ for rat 32 mg/kg	
$ZnSiF_4$	zinc silicofluoride					in water	LD ₅₀ for rat 100 mg/kg	
$MgSiF_4$	magnesium silicofluoride					in water	low toxicity	
Na_2SiF_4	sodium silicofluoride					in water	LD ₅₀ for rat 125 mg/kg	
NH_4HSiF_4	ammonium silicofluoride						LD of all silicofluorides to man 25-59g F	

Microbiodegradation of Library Materials

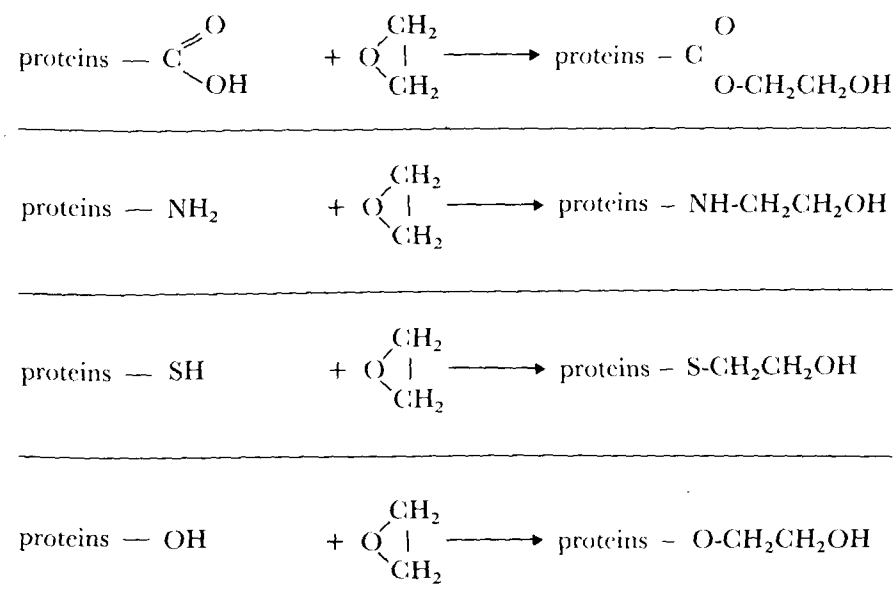
case moisture is not so important as concentration.^{21, 22, 23, 24} The mixture of ethylene oxide with carbon dioxide in the proportion 10:90 in a vacuum chamber is the most effective at 30–35% R.H. and becomes progressively slower as the relative humidity increases to 100%.^{3, 6, 16, 35} Not only is sterilization more difficult at relative humidities below 30%, but once microorganisms have been desiccated either chemically or by a vacuum, they require a resistance that is completely overcome when the relative humidity is again raised to 30%. Varying degrees of protection from ethylene oxide sterilization are afforded microorganisms embedded in water, oil, plastic and chemical crystals.^{16, 35}

The degree of protection imported to encased organisms depends on the type and thickness of plastic. It was found that cellophane and polyvinyl film have very low ethylene oxide permeabilities. Polyethylene is somewhat more permeable and ethylcellulose even more. Crystals of inorganic and organic salts provide complete protection to microorganisms from lethal action of ethylene oxide. It was shown,^{10, 11, 35, 42} that ethylene oxide could not sterilize internally contaminated, among others, calcium carbonate, which may influence the resistance of microorganisms, vegetating on parchment.

Generally speaking not all of the organisms are resistant, but a few maintain their resistance until they are essentially rewetted. Hydration of the species results increase in quantity of the fungicide absorbed. Besides that, physiological activity of microorganisms increase probably their sensitivity to a fungicide and spores lose resistance to fungicides in the early stages of germination, which is enlightened by relative humidity or moisture content of spores. The phenomenon of resistance to ethylene oxide is not well understood, but it is real and appears as a problem most often when one attempts to sterilize material that has been previously subjected to high vacuum or heat. Death time of the most resistant *Bacillus subtilis* at 54°C and 40–60% R.H. ranges 25 minutes for ethylene oxide sterilization process when gas concentration is 1000 mg/l and 2200 mg/l of ethylene oxide is needed at 21°C.^{5, 6, 47} In our experiments the most resistant fungi species were the following: *Chaetomium globosum*, *Trichoderma viride*, *Fusarium sp.*, *Penicillium sp.* and some *Actinomyces*. Ethylene oxide, as we have also found, does not influence negatively upon the paper, it does not change the acidity of paper and does not decrease its mechanical properties. Considering biocidal action, ethylene oxide causes a general disruption of biological processes. The exact site of alkylation produced by this compound is obscure. Two possibilities arise:

- a. mutagenic effect, involving effect on DNA (desoxyribonucleic acid) and therefore causes a lethal mutation, and

- b. alkylation of various essential proteins, such as enzyme⁴³ or ether or thioether formation in the proteins.¹⁵



According to these equations the reactions do not require water. However the destructive effect of ethylene oxide is significantly enhanced by 10–20% R.H.

The advantages of ethylene oxide sterilization lie not only in the speed, simplicity or economy of the treatment, but also in the fact that many types of materials are sterilized with least damage (with the exception of parchment and some other products) to the material itself using this technique. Ethylene oxide should be used especially carefully on rubber products,⁵³ leather objects and artificial materials, because they strongly absorb liquid ethylene oxide (1 g rubber absorb 0.6 g ethylene oxide). The utilization of ethylene oxide disinfection is as important for library materials (decrease of infection) as for the persons in contact with infective books or archives. There exists a danger for curators, stores superintendents and persons that must remain in spaces heavily contaminated with paper decomposing microflora. Apart from that we know that consumptive patients, for instance, spread infection by means of the minute droplets of tuberculous sputum sprayed in the act of coughing, sneezing and speaking. Some people have still the habit of wetting the thumb to facilitate the turning of pages of the books and records. Moreover the bacteria, fungi and

other organisms may be infected by hands from handling the handkerchiefs of ill people and touching the books. In this way the infection of cholera disease due to mail from India to Europe and at the end of the 19th century during the epidemic, a strict injunction was imposed on lending the books from public libraries. The spore-bearers remain for long periods on the surfaces of book papers. Besides that, soft crude paper appears to be capable of holding more microbial growth than partially or highly glazed papers.⁷ It was given that tuberculous bacteria may retain in books in moist sputum 9–10 months and in dried sputum 3 months.³⁸ *Streptococcus scarlatinae* survive on inoculated books for a period of four weeks. *Corynebacterium diphtheriae* retained on books 7 days and *Pneumococcus* 10 days. *Pseudomonas aeruginosa*, observed also on books, retained there several days. Therefore the disinfection seems to be essential, when considering this point of view. Ethylene oxide as was found ^{cit. 27} decontaminates books and archives infected with various bacteria including *Mycobacterium tuberculosis*.

One of the greatest drawbacks to the use of ethylene oxide as a sterilant is its slow action. Two methods are used by manufacturers to speed up its activity by the use of heat and increased pressure. A method of potentiating the activity of ethylene oxide gas by formic acid vapour was patented.¹⁸ The two chemical treatments are performed separately to avoid a chemical reaction. The method is claimed to potentiate the activity of epoxides so that their rate of action against microorganisms is increased and they are made effective under circumstances where they do not at present exert a sterilizing activity, namely, on very dry materials.¹⁶ The mixture of 40% ethylene oxide and 60% methyl bromide (weight per volume) is proposed, as more bactericidal than particular components. Moreover, the mixture is nonflammable because of the methyl bromide.⁵¹ Methyl bromide together with ethylene oxide is proposed to disinfect and disinfest the manuscripts.⁴⁵ It is worth mentioning that methyl bromide in the concentration of 11,000 ppm in the fumigation tent⁵⁰ caused severe intoxication in one man. After intoxication he had headache, loss of appetite and general spasms with urinary incontinence and coma. In hospital he had 38.6°C temperature and pulmonary edema with chemical pneumonia. He recovered consciousness after 28 days in hospital with appearance of illusions and persecution mania. After one year after fumigation he displayed emotional instability and tremor and he was deaf and unable to eat without help.

Coming back to ethylene oxide it cannot ensure the durable protection against microflora and even before lamination the use of long lasting biocide to the paper or tissue seems to be necessary as owing to Kerner-Gang³⁵ the spores of some fungi as *Penicillium sp.* and *Trichoderma viride* were not killed by the

temperature and pressure conditions of Barrow lamination. Dichlorophene has been proposed by us to treat Japanese tissue when using it with cellulose acetate to repair damaged paper.

At the end of this section I should like to add that the morpholine process for deacidifying whole books seems to have biocidal effects on fungi according to first attempts made by a Corning Museum microbiologist in 1973.⁵²

4.4.2 Abstract

Decomposition of Paper by Microorganisms

After World War II, library and archival materials in Poland were deteriorated as a rule by microorganisms and at a present time particular environmental conditions favour fungus growth. Many fungi and some other microbial agents have been isolated and identified and biochemical activity of some of them has been studied. Numerous fungi- and bactericides proposed for the protection of paper were evaluated, considering also some microbiocides in a vapour form. Fungicides destined for permanent preservation of old papers and manuscripts have been also tested.

More attention was paid to the biocide utilized for the immediate killing of microorganisms, but not immunizing cellulosic objects.

4.4.2 Résumé

Décomposition du papier par action microbienne.

Après la deuxième Guerre Mondiale, les matériels de bibliothèque et d'archive en Pologne furent en général l'objet de détériorations par les microorganismes, alors qu'à l'heure actuelle des conditions particulières de l'environnement favorisent la croissance des moisissures. De nombreuses moisissures et quelques agents microbiens ont été isolés et identifiés, l'activité biochimique de certains d'entre eux a été étudiée. De nombreux fongicides et bactéricides recommandés pour la protection du papier ont fait l'objet d'investigations de même que certains agents antimicrobiens à l'état gazeux. Les fongicides conçus pour la conservation permanente de papiers et de manuscrits anciens ont aussi fait l'objet d'essais.

Une attention spéciale s'est portée sur un produit biocide ayant un effet bactéricide immédiat sur les microorganismes sans immuniser les objets à base de cellulose.

4.4.2 Resümee

Zersetzung von Papier durch Mikroorganismen.

Nach dem 2. Weltkrieg wurden Bücherei- und Archivbestände in Polen in der Regel durch Mikroorganismen beschädigt. Gegenwärtig fördern bestimmte milieubedingte Voraussetzungen das Wachstum von Pilzen. Viele Pilze und andere mikrobiologische Elemente sind isoliert und identifiziert worden, die biochemische Tätigkeit einiger dieser Pilze und Mikroorganismen ist untersucht worden. Zahlreiche Fungizide und Bakterizide für den Schutz von Papier sind beurteilt worden, darunter auch einige Mikrobiozide in Form von Dampf.

Daneben sind auch Fungizide, die für den permanenten Schutz von alten Papieren und Manuskripten bestimmt sind, getestet.

Grosse Aufmerksamkeit wurde dem Biozid gewidmet, das zur sofortigen Abtötung von Mikroorganismen verwendet wird, das jedoch nicht Zellulose-Gegenstände immunisiert.

4.4.3 References

1. Barrow, W. J.: Permanence/Durability of the Book. VII. Physical and Chemical Properties of Book-Papers 1507-1949. W. J. Barrow Laboratory Inc.: Richmond, Virginia 1974.
2. Baynes-Cope, A. D. in Walters, A. H. & Hueck van der Plas, E. H. (eds.): *Biodeterioration of Materials*. Applied Science Publ., Ltd. London vol. 2 (1972): 381.
3. Block, S. S. in Lawrence, C. A. & Block, S. S. (eds.): *Disinfection, Sterilization and Preservation*. Lea and Febiger. Philadelphia 1968: 575.
4. Block, S. S.: *Experiments in Mildew Prevention*. Engineering Progress at the University of Florida VI: 4 (1952): 27-31.
5. Bruch, C. W.: *Gaseous Sterilization*. Annual Review of Microbiology 15 (1961): 245-262.
6. Bruch, C. W.: *Biological Indicators and Degrees (Probabilities) of Sterilization*. Development of Industrial Microbiology 14 (1973): 3-16.
7. Bryan, A. H.: *Book Contamination by Bacteria*. Industrial Medicine 6: 2 (1937): 73-74.
8. Cunha, G. M.: Conserving Local Archival Materials. Technical Leaflet 30 (11.) November 1975.
9. Cunha, G. M.: *An Evaluation of Recent Developments for the Mass Drying of Books* In Williams, J. C. (edit.) *Preservation of Paper and Textiles of Historic and Artistic Value*. Advances in Chemistry. Series 164 (1977). American Chemical Society. Washington: 95-104.
10. Doyle, J. E. & Ernst, R. R.: *Resistance of Bacillus subtilis var. niger Spores Occluded in Water in Soluble Crystals to Three Sterilizing Agents*. Applied Microbiology 15 (1967): 726-730.
11. Ernst, R. R. & Doyle J. E.: *Sterilization with Gaseous Ethylene Oxide. A Review of Chemical and Physical Factors*. Biotechnology and Bioengineering 10 (1968): 1-31.
12. Fischer, D. J.: *Simulation of Flood for Preparing Reproducible Water-Damaged Books and Evaluation of Traditional and New Drying Processes*. In Williams, J. C. (edit.) *Preservation of Paper and Textiles of Historic and Artistic Value*. Advances in Chemistry Series 164. American Chemical Society. Washington 1977: 105-123.
13. Fischer, D. J.: *Conservation Research. Use of Dielectric and Microwave Energy to Thaw and Dry Frozen Library*. In Williams, J. C. (edit.) *Preservation of Paper and Textiles of Historic and Artistic Value*. Advances in Chemistry Series 164. American Chemical Society. Washington 1977: 124-138.
14. Fischer, D. J.: *Conservation Research: Fumigation and Sterilization of Flood Contaminated Library, Office, Photographic and Archival Materials*. In Williams, J. C. (edit.) *Preservation of Paper and Textiles of Historic and Artistic Value*. Advances in Chemistry Series 164. American Chemical Society. Washington 1977: 139-148.
15. Fraenkel-Conrat, H. L.: *Action of 1,2-Epoxydes on Proteins*. Journal of Biological Chemistry 154 (1944): 227-238.
16. Gaughran, E. R. L.: *Newer Methods and Trends in Sterilization*. Development in Industrial Microbiology 14 (1973): 57-64.
17. Hetherington, D. C.: *Mold Preventive for Book Bindings*. Science 101 (1945): 223.
18. Kaye, S.: USPat. 3257161 (1966).
19. Kaye, S.: *New, non-Damaging Preventatives of Biodeterioration-Monochloroacetate Esters of Chlorinated Phenols*. Development in Industrial Microbiology 17 (1976): 159-165.
20. Kennedy, R. A.: *Conservation in Wet Tropics*. Museum Association of Middle Africa. Technical Bulletin 1 (1959).
21. Kereluk, K. & Gammon, R. A.: *The Microbiocidal Activity of Ethylene Oxide*. Development in Industrial Microbiology 14 (1972): 28-41.
22. Kereluk, K., Gammon, R. A., Lloyd, R. S.: *Microbiological Aspects of Ethylene Oxide Sterilization. I. Experimental Apparatus and Methods*. Applied Microbiology 19: 1 (1970): 146-151.
23. Kereluk, K., Gammon, R. A., Lloyd, R. S.: *Microbiological Aspects of Ethylene Oxide Sterilization. II. Microbial Resistance to Ethylene Oxide*. Applied Microbiology 19: 1 (1970): 152-156.
24. Kereluk, K., Gammon, R. A., Lloyd, R. S.: *Microbiological Aspects of Ethylene Oxide Sterilization. III. Effects of Humidity and Water Activity of Ethylene Oxide*. Applied Microbiology 19: 1 (1970): 157-162.
25. Kerner-Gang, W.: *Mikrobiologische Untersuchungen an Eingesiegelten Archivalien*. Material und Organismen 9: 1 (1974): 13-20.
26. Kowalik, R.: *Some Problems of Microbiological Deterioration of Paper*. Annali della Scuola Speciale per Archivisti e Bibliotecari dell'Universita di Roma. Nuova Tecnica Grafica. Roma 1-2 (1972): 61-80.
27. Kowalik, R.: *Some Aspects of Microbiology of Paper and Parchment* In Petersen, D. E. (edit.) *Herzog August Bibliothek Wolfenbütteler Forschungen*. Jacobi Verlag. Bremen und Wolfenbüttel Band 1 (1977): 61-90.
28. Kowalik, R. & Czerwińska, E.: *Wybrane Zagadnienia Mikrobiologii Technicznej. Podstawowe Problemy Współczesnej Techniki*. Polska Akademia Nauk. Warszawa 1971: 17-67.
29. Kowalik, R., Sadurska, I., Czerwińska, E.: *Microbiological Deterioration of Old Books-Remedies*. Bolletino dell'Istituto di Patologia del Libro "Alfonso Gallo" 21 (1962): 116-151.
30. Kowalik, R., Sadurska, I., Czerwińska, E.: *Zniszczenia Papieru przez Mikroflorę*. Blok-Notes Muzeum Mickiewicza 2 (1963): 259-312.
31. Martin, J. H. (edit.): *Museum under Water-The Corning Flood*. The Corning Museum of Glass. Corning, New York 1977.
32. Mac Donald, R. G. & Franklin, J. N. (eds.): *Pulp and Paper Manufacture*. McGraw Hill Book Co. New York 1970: 104.
33. Middleton, B. C.: *Book Preservation for the Librarian*. In Williams, J. C. (edit.) *Preservation of Paper and Textiles of Historic and Artistic Value*. Advances in Chemistry Series 164. American Chemical Society. Washington D. C. 1977: 3-23.
34. Monro, H. A. U.: *Manual of Fumigation for Insect Control*. FAO of the United Nations. Rome 1969.
35. Mullican, C. L. & Hoffman, R. K.: *Dry Heat or Gaseous Chemical Resistance of Bacillus subtilis var. niger Spores Included Within Water-soluble Crystals*. Applied Microbiology 16 (1968): 1110-1113.
36. Munakata, K., Kuwahara, M.: *Photochemical Degradation Products of Pentachlorophenol*. Residue Reviews 25 (1969): 13.
37. Nordstrand, O. K.: *Chinese Double-leaved Books and their Restoration*. Libri 17 (1967): 104-130.
38. Omeliański, W. L.: *Izbrannyje Trudy vol II*. Izdatielstwo Akademii Nauk SSSR. Moskwa 1953: 318.
39. Opfell, J. B. & Miller, C. E.: *Cold Sterilization Techniques*. Advances of Applied Microbiology 7 (1965): 81-102.
40. Plenderleith, H. J. & Werner, A. E.: *The Conservation of Antiquities and Works of Art*. London-Oxford University Press 1974.
41. Reed, R.: *Ancient Skins, Parchments and Leathers*. Seminar Press London and New York 1972.
42. Royce, A. & Bowler C.: *Ethylene Oxide Sterilization-Some Experiments*. Journal of Pharmacy and Pharmacology 13 (1961): 87 T-94 T.
43. Russell, A. D.: *The Destruction of Bacterial Spores* In Hugo, W. B. (edit.) *Inhibition and Destruction of the Microbial Cell*. Academic Press. New York 1971: 451-612.

Microbiodeterioration of Library Materials

44. Shumard, R. S.: *Mildew Control. Possibilities of para-Dichlorobenzene as an Aid in Preventing Damage by Mildew*. Soap 29 (1953): 150-151, 153, 171-173.
45. Smolkina, T. N.: Zashchita Dokumentov ot Biopowriedienija s Primienienijem Gazowowo Mietoda Dezynfekcji i Dezynsekcji. Wsiesojuznyj Nauczno-Issledowatielskij Institut Dokumentowiedienija i Archiwnowo Dieła. Głównoje Archiwnoje Uprawlenije pri Sowietie Ministrow SSSR. Moskwa 1975.
46. Stanojlowic, L.: Mesure d'Intervention en Cas de Desastré ou Creation d'un Centre National d'Intervention et de Sauvetage en Cas d'Urgence. ICOM Committee for Conservation Zagreb 78 (1978): 14: 3.
47. Sykes, G.: *The Sporocidal Properties of Chemical Disinfectants*. Journal of Applied Bacteriology 33 (1970): 147-156.
48. Torkelson, T. R., Hoyle, H. R., Rowe, V. K.: *Toxicological Hazards and Properties of Commonly used Space, Structural and certain other Fumigants*. Pest Control 34: 7 (1966): 13-14.
49. Toskina, I. N.: Diejstwije para-Dichlorobenzola na Materialy Upotriebljajemyje w Akwarelnoj Žiwopisi. Soobszczenija Wsiesojuznoj Cienralnoj Nauczno Issledowatielskoj Laboratorii Konserwacji i Restawracji 30 (1975): 9-15.
50. Ushio, K. & Osozuka, R.: *A Case of severe Intoxication due to Methyl Bromide*. Sangyo Igaku 19: 5 (1977): 355-356.
51. Vashkov, V. I. & Prishchep, A. G.: *Efficiency of Sterilization by Making Use of Ethylene Oxide and Methyl Bromide Mixture* In Brown, A. H. & Florki, M. (eds.) Life Science and Space Research. North Holland. Amsterdam VI (1967): 44-50.
52. Walker, B. F.: *Morpholine Deacidification of Whole Books* In Williams, J. C. (edit.) Preservation of Paper and Textiles of Historic and Artistic Value. Advances in Chemistry Series 164. American Chemical Society. Washington 1977: 72-87.
53. Wallhäuser, K. H. & Schmidt, H.: *Sterilisation, Desinfektion, Konservierung, Chemotherapie*. G. Thieme Verlag. Stuttgart 1967.
54. Waters, P.: *Procedures for Salvage of Water-Damaged Library Materials*. Library of Congress. Washington 1975.
55. Werner, A. E.: Private Communication.
56. Zappala, M.: *Some Aspects of the Chemical Research in the Istituto di Patologia del Libro* In Conservation of Paintings and the Graphic Arts. Lisbon Conference 1972: 995-1000.

4.5.1 Decomposition of Parchment by Microorganisms

Some products of animal origin are more firm and more durable than cellulosic materials. These are parchment and leather, possessing as a basic component collagen, protein composed of aminoacids of high molecular weight approximately 310,000-350,000.^{10, 14} The use of parchment reaches far back into ancient eras, and according to Herodotus, sheep and goats were used in antiquity for this purpose.⁹ Parchment as writing material was produced from sheepskin or more delicate and white lambskin. Better qualities of parchment are attributed to deer and antelope⁹ and particularly valuable parchment was made from embryos of lambs and calves.⁹ In ancient times goats, lambs,

sheep and animal intestines have been used for the manufacture of parchment. To remove the impurities the skins for parchment were held two or three days in water, then limed, dehaired and very thoroughly defleshed. The skins were sometimes also subjected to a putrefying process, rinsing in pure running water and treating with mild organic acids, as whey, sour beer, wine and honey. In order to correct the elasticity enzymic maceration was carried out by using excrements of hen, dogs, pigeons or by mincemeat made of pigs intestines, containing trypsin. Parchment, after drying off was polished with a pumice block. The essential characteristics of parchment are: whiteness, elasticity, strength and complete lack of fat.

Parchment is composed of collagen, some amounts of keratin and elastin, and minimal amounts of albumin and globulin. The basic component of collagen^{8, 14} is not a pure protein and contains about 0.65% of polysaccharides, composed of galactose and glucose. Sheepskin, most often used for parchment contains an abundance of fats (31%) in form of waxes, triglycerides, phospholipids and fatty acids occurring due to hydrolysis.⁸

During the process of parchment manufacture, lime soap difficult to remove is precipitated. Moreover skin tissues contain numerous vitamins. All these substances might well function as nutrients for the microorganisms that attack parchment, although the basic component collagen is microbioresistant in aerobic conditions and is hydrolyzed only by specific collagenases produced by anaerobic bacteria of the genus *Clostridium*-*Clostridium histolyticum*, *Clostridium perfringens* and *Clostridium capitovale*.^{6, 16} No data are available regarding synthesis of collagenase by aerobic bacteria up to 1973¹⁶ when Woods *et al.* isolated collagenolytic bacteria *Achromobacter iophagus*.¹⁶ Denaturated collagen of course may be decomposed by bacteria of the genus *Pseudomonas*, *Bacteroides*, *Bacillus* as *Bacillus licheniformis*, and mentioned *Achromobacter*.^{13, 16} Adamcic and Clark¹ have shown that the components of the fractions alpha, beta and gamma collagen, soluble in alkaline salt, have been attacked after 4-6 days of culture by coloured species of *Pseudomonas*. These authors attribute previous negative results to too short a period of culture (one day).

The degree of susceptibility of parchment to the attack of microorganisms depends on the raw material, its method of production and on the conditions of its preservation. Violent changes of humidity and temperature and exposure to the action of UV^{2, 3, 8, 10} may cause changes in the structure of collagen-partial depolymerization. As a consequence of the activity of these agents, its resistance against microorganisms is lowered. It is worthwhile to emphasize that disinsection and disinfection of library materials by means of ethylene oxide also causes the denaturation of collagen^{8, 10} and may influence the decrease of microbial resistance.



Fig. 1. *Cladosporium herbarum* ($\times 500$).

Studies of the microflora of parchment have been carried out by some authors.^{7, 10, 11} Smirnowa¹¹ and Szoc¹² have isolated many species of microorganisms and have confirmed that microorganisms cause spoilage of parchments. Parchment, according to these data, is attacked by certain species of the genus *Penicillium*, *Aspergillus*, *Alternaria* and *Cladosporium*. The most deleterious effect on parchment occurred under the influence of some strains of *Streptomyces*, *Cladosporium*, *Fusarium*, *Ophiostoma* and *Scopulariopsis*.^{8, 10, 12} (Figs. 1-5).

Taking into consideration all these experiments, the conclusion was drawn that parchment ought to be protected by the use of microbiocides. Selection, however is difficult owing to the physicochemical properties of the parchment membrane and some *ad hoc* studies seemed to be called for.

According to the scanty information available the growth of microorganisms on parchment is inhibited by the following biotoxins: 4-chloro-3-cresol, thymol, formaldehyde and trichlormethylene.^{5, 8} From my point of view, out of the fungicides mentioned, only 4-chloro-3-cresol may be used for the protection of parchment for the following reasons: It is the most potent fungitoxicant and



Fig. 2. *Scopulariopsis brevicaulis* ($\times 1500$).

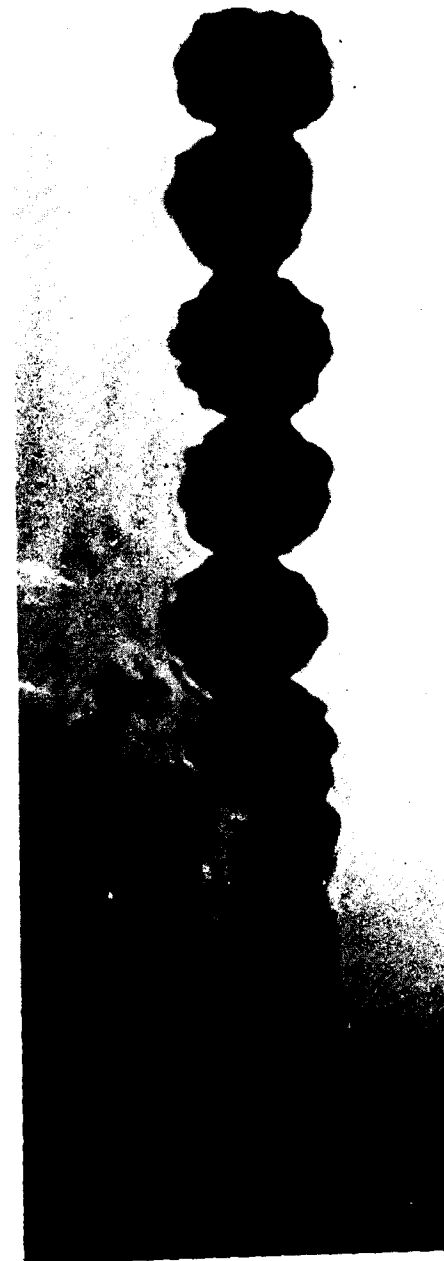


Fig. 3. *Scopulariopsis brevicaulis* ($\times 3000$).

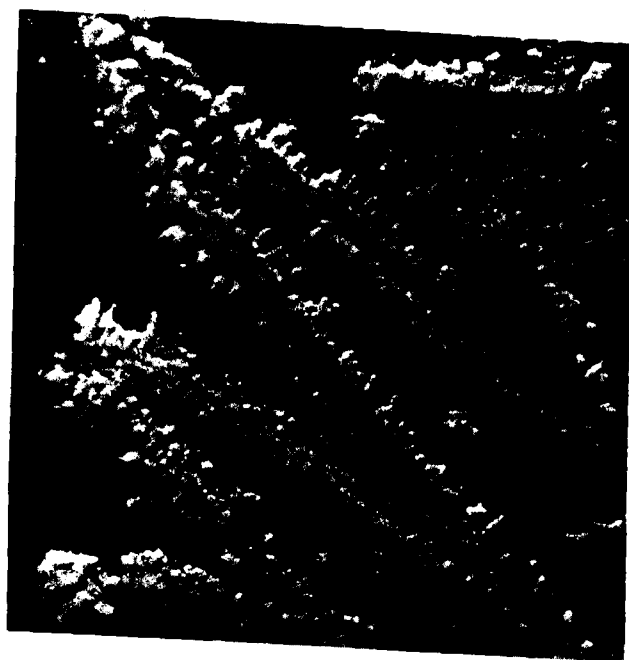


Fig. 4. Growth of *Streptomyces* sp. on the back of parchment.

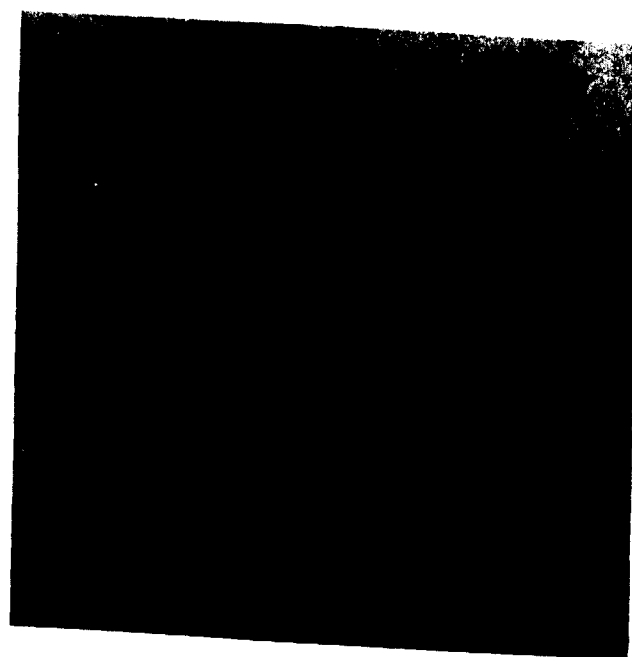


Fig. 5. Growth of *Cladosporium herbarum* on the face of parchment.

it is also bacteriostatic and has a good relationship with collagenic materials. Besides this it is less toxic to humans than any of the other compounds. From among the others, thymol is too shortlived and formaldehyde has a deleterious effect on parchment because it hardens it and tends to give rise to a blue colouration;^{2, 3} trichlormethylene seems to be only insect fumigant.

In our studies^{8, 10} parchment deteriorating microorganisms were isolated by the following procedures:

Samples of parchment were washed with sterilized distilled water and were placed in Petri dishes, hair and flesh side to the surface of hardened agar medium (20 g of agar-agar and 1000 ml of distilled water) and to the gravel soaked with distilled water of pH = 5.6 without any other additional food nutrients. Cultures were carried out during 3 weeks at the temperature 24–26°C and 85–90% R.H.

Appearing colonies of microorganisms were isolated by transferring them to the test tubes with agar. The ability of the isolated organisms to decompose parchment was tested too. To this purpose samples of the parchment, the thickness of which varied between 0.2–0.4 mm, depending upon the place of measurement, were inoculated with particular isolated previously parchment-deteriorating microorganisms. Cultures were carried out for 3 weeks at the temperature and R.H. as mentioned above. The samples were then picked out from the agar and after washing to remove mycelium loss of tissue was visually determined. When the amount of experimental material was sufficient in quantity the mechanical resistance was evaluated by dynamometer. Samples of parchment of size 20 × 100 mm were tested in the dynamometer to 100 kg/cm² at a velocity of tear resistance 80 mm/sec.

From the tested parchment several species of *Streptomyces* and the following fungi were isolated: *Alternaria* sp., *Aspergillus niger*, *Aspergillus* sp., *Chaetomium globosum*, *Cladosporium herbarum*, *Fusarium orthoceras*, *Fusarium* sp., *Gloeosporium* sp., *Ophiostoma* sp., *Sepedonium* sp., *Scopulariopsis brevicaulis* and *Sporendonema* sp.

It was found that the strains of *Streptomyces* occurred the most often. On the parchment prepared by my student, M. Szoc, several strains of *Fusarium* also appeared. On the 19th century parchment *Ophiostoma* and some species of bacteria were identified and on Italian parchment samples, which I have received from dr. Fausta Gallo, *Scopulariopsis* and *Sporendonema* were isolated.

The growth of these microorganisms was more intensive on the flesh than on the hair side of these parchments, which were found to be decomposed by the majority of the microorganisms that were isolated.

Streptomyces sp., *Cladosporium herbarum* and *Sporendonema* caused loss of membrane tissue and *Fusarium orthoceras*, *Ophiostoma* sp. and *Scopulariopsis brevicaulis* gave rise to coloured spots and attenuation of the tissue.

Microbiodeterioration of Library Materials

Tests of the mechanical properties have shown that the decrease of tear resistance of the Italian parchment subjected *Streptomyces* amounted to 57.0%, *Cladosporium* to 51.0% and *Fusarium* to 63.0%. The 19th century parchment of pH = 6.1 was completely destroyed by these microorganisms.

The influence of ethylene oxide and carbon dioxide was established on the 19th century parchment of pH = 5.8 after obtaining the vacuum of 10 mm Hg in a vacuum chamber and under pressure of 1 atmosphere for 4 hours during two successive days. It was found that neither the gaseous mixture of ethylene oxide and carbon dioxide used in a vacuum chamber nor the vacuum itself lowered the mechanical resistance of parchment. Tear resistance of treated and check samples was nearly of the same order. The mixture of ethylene oxide and carbon dioxide, however, negatively influenced the biological resistance. The samples that had been treated with the gaseous mixture and inoculated thereafter with microorganisms developed mycelium earlier and more heavily than inoculated controls that had not been gassed.¹⁰

Parchment exposed to ethylene oxide and contaminated with air microflora was infected more heavily and by more numerous species of microorganisms than parchment not disinfected and subjected to a vacuum effect. The mechanism by which ethylene oxide kills microorganisms has been linked to its chemical activity due to alkylation of hydroxyl, carbonyl, sulphhydryl and imino groups in protein molecules with the loss of labile hydrogen atom and the production of an alkyl hydroxyethyl group. If ethylene oxide reacts with active sites of protein molecules we may expect that similar reactions would occur with these groups where they exist in materials (for instance depolymerized collagen of parchment) being sterilized as well as in the constituent molecules of microorganisms. Thus we can, from my point of view, explain the damage caused by ethylene oxide sterilization and even anticipate it in protein materials, especially parchment and maybe adhesives and others.

From the tests of several biocides: *o*-phenylphenol, dichlorophen, 4-chloro-3-cresol and pentachlorophenol and the mixture of the two last fungicides, it was found that only the mixture of 0.5% of 4-chloro-3-cresol and 0.5% of pentachlorophenol (1:1) completely protected parchment against microorganisms when used in the amount of 2 ml to 100 cm². Pentachlorophenol has, however, several disqualifying characteristics (decomposition in the light). It is advised therefore to use only 4-chloro-3-cresol which protects parchment against microflora from the air. After inoculation with well fructifying fungi isolated from parchment the treatment with 0.5% of 4-chloro-3-cresol is not sufficient.^{8, 10}

It is worth mentioning that Belaya⁴ described a method of softening dry deformed parchment by treating it with a 10% solution of urea in ethyl alcohol

benzene emulsion of spermaceti; the latter increases the strength and elasticity of the parchment. This treatment does not increase the hygroscopicity of the parchment and has no deleterious effects on the text or illumination in parchment manuscripts. Werner¹⁵ advises as sizing for parchment Calaton CB(*n*-methoxymethylnylon) 2% solution by using it with the help of a camel hair brush. This non-shiny compound returns the original strength to brittle documents and manuscripts on parchment. Werner used this form of nylon for consolidation of the frescoes from the tomb of Thebes. According to our experiments *n*-methoxymethylnylon is completely microbioresistant.

At the end of this chapter it is worth mentioning that parchment may be sealed in a glass container which, being inert chemically, has an advantage over plastics. Polystyrene, polypropylene and polymethacrylate may lead to crazing and fine crack formation.¹⁷

*4.5.2 Abstract**Decomposition of Parchment by Microorganisms*

Parchment subjects microbiological deterioration depending upon raw material, methods of production and on the conditions of its preservation. The most active microbial agents against parchments are the following: *Streptomyces*, *Cladosporium*, *Scopulariopsis*, *Fusarium*, *Sporendonema* and *Ophiostoma*.

Ethylene oxide with carbon dioxide in a vacuum chamber shows that parchment is prone to more speedy decomposition by microorganisms. It is advised to use 4-chloro-3-cresol as a fungicide that protects parchment against contamination of microorganisms from the air.

*4.5.2 Résumé**Décomposition du parchemin par action microbienne.*

Les documents en parchemin sont l'objet de détériorations microbiennes qui sont fonction de la matière première utilisée, des méthodes de production et des conditions de conservation. Les espèces microbiennes les plus actives vis-à-vis du parchemin sont les suivantes: *Streptomyces*, *Cladosporium*, *Scopulariopsis*, *Fusarium*, *Sporendonema* et *Ophiostoma*.

L'oxyde d'éthylène et le gaz carbonique en chambre à vide prouvent que le parchemin a tendance à se décomposer plus rapidement sous l'action des microorganismes. L'emploi de 4-chloro-3-crésol comme fongicide est recommandé du fait de la protection du parchemin contre la contamination par les microorganismes de l'air.

*4.5.2 Resümee**Zersetzung von Pergament durch Mikroorganismen.*

Die mikrobiologische Zerstörung, der Pergament ausgesetzt ist, hängt vom Rohmaterial, den Produktionsmethoden und den Konservierungsbedingungen ab. Folgende Mikroorganismen greifen Pergament am aktivsten an: *Streptomyces*, *Cladosporium*, *Scopulariopsis*, *Fusarium*, *Sporendonema* und *Ophiostoma*.

Äthylenoxid und Kohlendioxid in einer Vakuumkammer zeigen, dass Pergament zu einer schnelleren Zersetzung durch Mikroorganismen neigt. Es wird empfohlen, 4-Chlor-3-Kresol als Fungizid zu verwenden, um Pergament gegen den Angriff durch Mikroorganismen aus der Luft zu schützen.

4.5.3 References

1. Adamcic, M. & Clark, D. S.: *Collagenolytic activity of pigmented Pseudomonads*. Canadian Journal of Microbiology 16 (5) (1970): 709–713.
2. Baynes-Cope, A. D.: *The Conservator's point of view. Microbiological Deterioration in the Tropics*. Society of Chemical Industry Monograph No. 23. London 1966: 121–124.
3. Baynes-Cope, A. D. In Walters, A. H., Hueck van der Plas, E. H. (eds.): *Biodeterioration of Materials*. Applied Science Publ. Ltd. London vol. 2 1972: 381.
4. Belaya, I. K.: *Softening and Restoration of Parchment in Manuscripts and Bookbinding*. Restaurator 1 (1969): 20–48.
5. Block, S. S. In Lawrence, C. A. & Block, S. S. (eds.): *Disinfection, Sterilization and Preservation*. Lea and Febiger. Philadelphia 1968: 575.
6. Eddy, B. P.: *Microbial Spoilage* In Rainbow, C. & Rose, A. H. (eds.): *Biochemistry of Industrial Microorganisms*. Academic Press. London 1963: 489.
7. Gallo, F.: *Insetti e microorganismi dei libri*. Bollettino dell Istituto di Patologia del Libro 26 (1967): 143–190.
8. Kowalik, R.: *Some Aspects of Microbiology of Paper and Parchment*. Wolfenbütteler Forschungen 1 (1977): 61–90.
9. La Lande, M. de: *Art de faire le parchemin*. Descriptions des Arts et Métiers. Saillant et Nyon. Desaint. Paris 1762: 1–52.
10. Sadurska, I. & Kowalik, R.: *Protection of Parchment against Microflora*. Annali della Scuola Speciale per Archivisti e Bibliotecari dell'Università di Roma. Nuova Tecnica Grafica. Roma 9 (1969): 51–60.
11. Smirnowa, B. I.: *Waprosy Konserwacji Bumagi i Piergamena*. Akademija Nauk SSSR. Moskwa 1962.
12. Szoc, M. (unpublished data).
13. Tardieux, M., Moussin, M. H., Flieder, F., Pochon, M. J.: *Altération biologique des parchemins*. Comptes Rendus de l'Académie des Sciences. Paris 272 (1971): 1817–1818.
14. Walton, A. G. & Blackwell, J.: *Biopolymers*. Academic Press, New York, London 1973: 415.
15. Werner, A. E. A.: *Neue Werkstoffe für Konservierungszwecke*. Maltechnik. 75 (1969): 101–106.
16. Woods, D. R., Rawlings, D. E., Cooper, D. R., Galloway, A. C.: *Collagenolytic activity of hide bacteria and leather decay*. Journal of Applied Bacteriology 36 (1973): 289–295.
17. Reed, R.: *Ancient Skins, Parchments and Leathers*. Seminar Press London and New York 1972.

4.6.1 Decomposition of Leather by Microorganisms

Leather was also used as writing material and this was quite common in Egypt⁸ and later on in other Near Eastern Countries.¹¹ Early use of animal skins is evident from the works of Herodotus, Dioscorides, Pliny and rabbinical literature produced by Jewish scribes as well as from Babylonian and Assyrian sources.

As a rule however leather has been utilized for bookbindings. Biological agents do not consume, generally, the basic component-collagen as the only source of carbon and nitrogen food, excluding insects and a few anaerobic⁷ and one aerobic bacteria.^{12, 15} We do not know how larvae and adult insects metabolize such a complicated polymer, but it might be possible that the insects possess anaerobic collagenolytic bacteria in the alimentary tract.

The susceptibility of bookbinding leathers to microbial agents depends on the type of leather, kinds of dyes and most of all on the method of tanning. Vegetable tanned leather has been shown to absorb acidic gases from city atmospheres and this kind of leather is also susceptible to microorganisms. But, on the other hand, only vegetable tannage may be used for library objects, because of the physical properties (better elasticity) of leather. To-day, satisfactory vegetable-tanned leathers based on strong skins, chosen from first quality goat or hair sheep, and tanned with sumac are available. However, the best materials to use for bookbinding according to Reed¹¹ are combination-tanned leathers based on chrome and vegetable tannages as semi-chrome leather or chrome pretanned vegetable leather. They have high water, heat and light stability and are certainly more bioresistant than vegetable tanned leather.

In addition to tanning agents, as acacia pods, oak bark, fruits, pathological excrescence on leaves, the leather contains products of tannins hydrolysis (2–28%) as sugars, gallic acid and other hydroxyacids, hemicelluloses and polyurea compounds.

Leather writing materials and bookbindings in libraries and museums are subject to microbial deterioration on exposure to humid, warm, spore-laden atmospheres. In the first place the growth is not primarily upon collagen-tannin complex, because collagen is microbioresistant with the exception of anaerobic conditions. Recently, besides anaerobic collagenolytic bacteria, as *Clostridium histolyticum* and *Clostridium capitovale*, collagenase producing aerobic bacteria *Achromobacter iophagus* was isolated. This bacteria also causes leather decay.^{12, 15} More readily attacked by proteolytic enzymes are the ends of the collagen molecules, telopeptides, which have non helical form in contrast to triple helical form of collagen. Telopeptide regions where the inter- and intramolecular bonds are found, show the loss of bonding and the cause that the

molecule and protein is less stable under the influence of enzymes, and the structure of leather is looser.⁵ Primarily, however, the principal components of leather which may be destroyed are the lubricant, the conditioning materials and the finish. Bacterial growth is rather an exception, since bacteria need approximately 100% R.H. and besides pH of the leather oscillates between 3 and 4, unsuitable for the growth of bacteria. Some collagenic materials contain also bacterial flora probably due to the depolymerization of collagen. As a rule, however, fungi and occasionally yeasts do grow abundantly on leather library objects and this may present a problem.

Fungi vegetating on leather cause the loss of greases and tannins and therefore there may be an increase in stiffness and decrease of tensile strength. The grain is also weakened and leather tends to crack. After removing the greases, sugars and to a certain degree tannins, leather's substance is fungi-resistant. Microorganisms may attack carboxylic group in fatty acids and the decarboxylation occurs. Fungi may also remove -COOH group from aminoacids, which may be transformed on amines, for instance alanine $\text{CH}_3\text{CHNH}_2\text{COOH}$ may be transformed by fungi in ethylamine $\text{CH}_3\text{CH}_2\text{NH}_2$. This process may occur especially in other proteins (excluding collagen) which may be present in leather objects.

Apart from proteins and lipids, microorganisms need to form cell material from other products. They may utilize carbohydrates and even tannins. Also, the microelements play an important role in the life of microflora, which may be found in leather in the form of impurities. Potassium, for instance, has an essential function in carbohydrate metabolism and growth and take an active part in the formation of cells dyes. Calcium is needed to neutralize oxalic acid, having harmful effects upon the growth of fungi. Calcium, together with zinc, influence the growth of most species of fungi. Sulfur, which in the form of sulfur dioxide may be absorbed by collagenic fibres particularly easily from atmosphere, is an indispensable element for the cell structure. Iron accelerates the respiration of microflora. Barium, borium, beryllium, iodine and silicium stimulate the growth of microorganisms too.

Microorganisms vegetating on leather belong first of all to fungi imperfecti. Philogenetically this group is one of the youngest on our continent and hence it could establish itself on a new food source as on tanned leather. Leather will support fungi growth at about 65% R.H., conditions too dry for many other products. The most occurring on leather fungi belong therefore to two groups: *Penicillium* and *Aspergillus* which tolerate comparatively low relative humidity. A very interesting leather-deteriorating fungus is *Aureobasidium pullulans*. It is a predominant blue stainer of wood, it decomposes paper pulp and manufactured

paper, it damages oil and water colour paintings, it causes changes of wool structure and nylon. It is also able to assimilate atmospheric nitrogen and may live in conditions very unsuitable for other microorganisms. It is resistant to high temperature, low humidity, intensive sunlight. Consequently *Aureobasidium pullulans* is a very harmful organism for library objects.

Yeasts and bacteria also occur on tanned leather. It may be added that some microorganisms possess the ability to produce coloured spots on leather bookbindings. Fungi dyes contrary to bacterial dyes are as a rule nonnitrogenous compositions. They contain quinones, which are oxidized and condensed. As a result of these processes the colour of the leather may be changed. To put it shortly, the attack of microorganisms on leather objects depends upon the carbon and nitrogen sources (tannins, adhesives and impurities), some vitamins and inorganic salts in small amounts, suitable relative humidity, moisture content, acidity and temperature. The presence of oxygen (excluding *Clostridium*) are also essential. The oldest methods of preservation of leather library objects is to maintain the R.H. between 50 and 63%, adequate ventilation and relatively low temperature near 15°C. These conditions, not always attainable, belong to passive conservation, where the object is not touched, and the surroundings of the object are altered or controlled to produce the maximum safety and durability of the object. The other aspect, according to Dr. Anthony E. Werner, depends upon active conservation and therefore, to protect leather objects against microflora, biocides are needed.

Much work has been done on preservatives for leather, but only a few have been used for valuable leather objects. Out of the phenol derivatives the following may be mentioned: 4-chloro-3-cresol, 4-chloro-3-xenol, *o*-phenylphenol, sodium trichlorophenate, sodium pentachlorophenate. Apart from these, esters of *p*-nitrophenol such as bis (*p*-nitrophenol) carbonate and bis (*o*-chloro-*p*-nitrophenol) carbonate were found to show approximately the same activity as the phenols, but were colourless which is a very important factor for valuable leather bookbindings and writing materials.

5.6-dichloro-2-benzoxazolinone was also found to have the desirable physical properties for the valuable objects from vegetable tanned leather. Octyl-4-izothiazolo-3-one (Kathon LP), 2,2'-dihydroxy-5,5'-dichlorodiphenyl monosulfide (Fenticlor) and dimethylthiono-tetrahydro thiodiazin (Dazomet DMF, Cosan S) may also be considered, as well as 2-(thiocyanomethylthio) benzothiazol (TCMTB, Busan 30), having broad spectrum of activity in a great pH range, low toxicity and water solubility. 100 ppm of Busan 30 protects leather 25 days in tropical conditions.

Phenylmercury acetate and phenylmercuric triethanol ammonium lactate

Table 2. The preservatives of leather.
Table 2. Agents de conservation du cuir.
Tabelle 2. Die Schutzmittel für Leder.

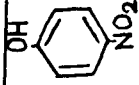
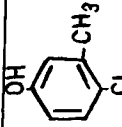
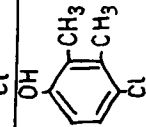
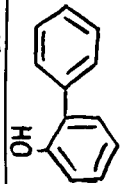
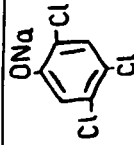
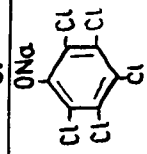
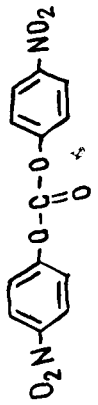
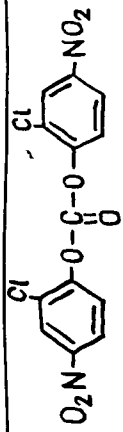
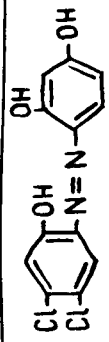
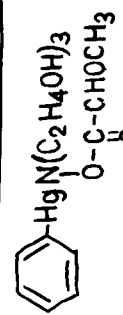
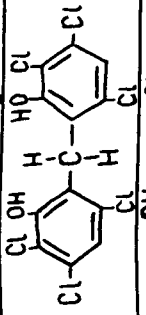
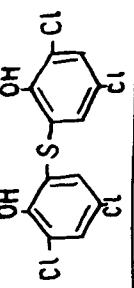
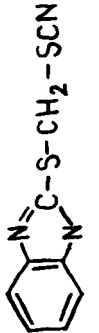
	p-nitrophenol
	4-chloro-3-cresol
	4-chloro-3-xylene
	o-phenyl-phenol
	sodium 2,4,5-trichlorophenolate
	sodium pentachlorophenolate
	bis(p-nitrophenol) carbonate
	bis(o-chloro-p-nitrophenol) carbonate
	5,6-dichloro-2-benzoxazolinone
	phenylmercuric acetate
	phenylmercuric triethanol ammonium lactate
	2,2'-methylenebis(3,4,6-trichlorophenol)
	2,2'-thiobis(4,6-dichlorophenol)
	2-(thiocyanomethylthio)benzothiazol

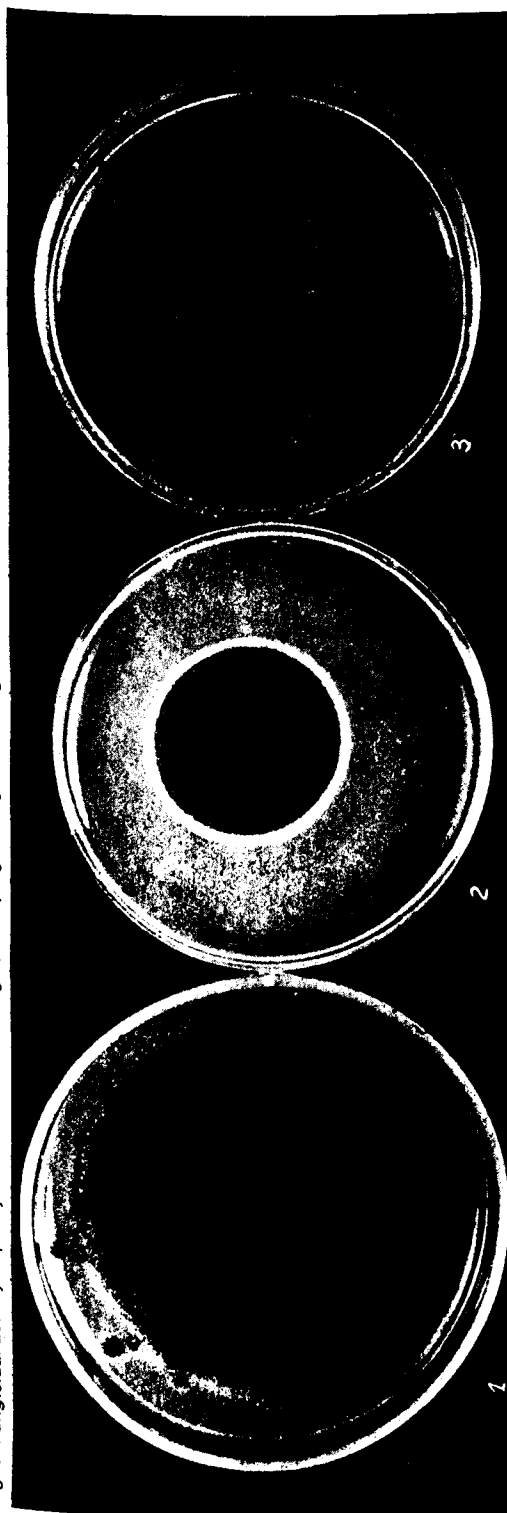


Fig. 2. *Penicillium* sp. ($\times 500$).



Fig. 1. *Aspergillus niger*, van Tieghem ($\times 500$).

Fig. 3. Fungicidal activity of phenyl mercuric acetate on agar, 'on *Aspergillus niger*, van Tieghem.



1: Control. 2: 0.00001% of fungicide. 3: 0.00001% of fungicide.

Fig. 4. Fungicidal activity of phenyl mercuric acetate on leather.



1: Control. 2: 0.0025% of fungicide. 3: 0.005% of fungicide.

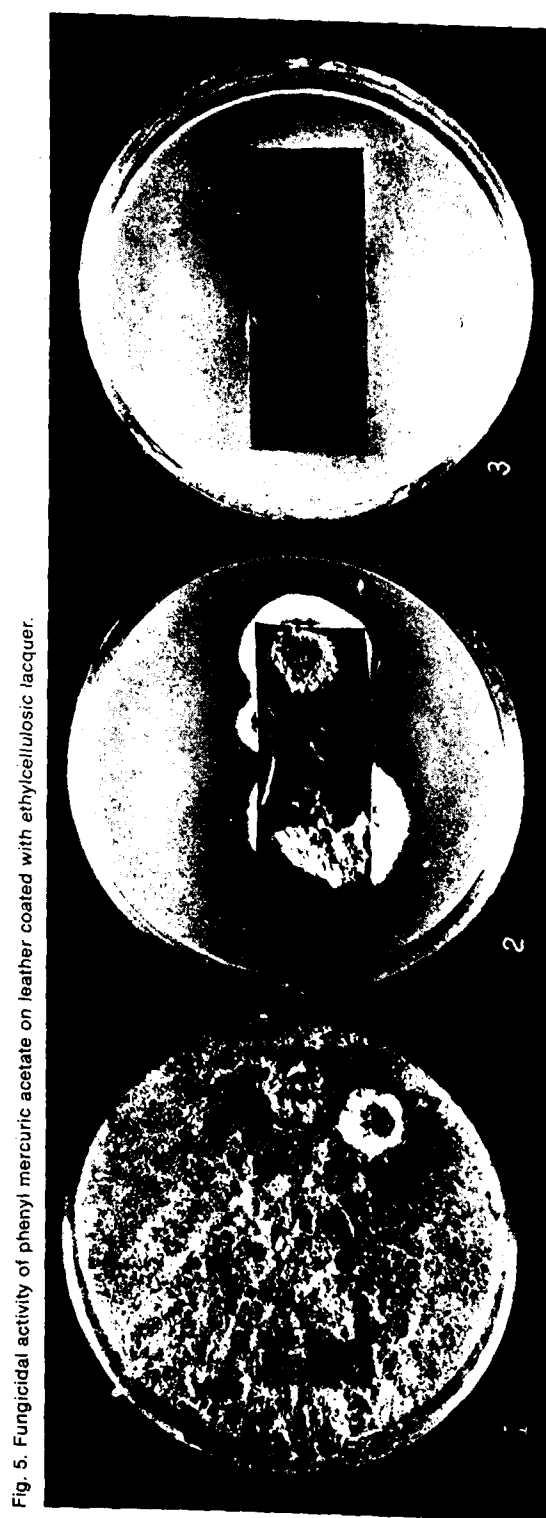


Fig. 5. Fungicidal activity of phenyl mercuric acetate on leather coated with ethylcellulosic lacquer.

1: Control. 2: 0.0025% of fungicide. 3: 0.005% of fungicide.



Fig. 6. Fungicidal activity of phenyl mercuric acetate on leather with dressing.

have been used in very low concentrations. Antibacterial properties suitable for library objects have 2,2'-methylene bis (3,4-6-trichlorophenol) (Hexachlorophene) and 2,2'-thiobis (4,6-dichlorophenol).^{2, 3, 4, 5, 6, 7, 9, 10, 13} (Tab. 2).

As we could observe, leather bookbindings chosen with the greatest care after consultations with binders and manufacturers seem liable to disintegrate in the course of many years. From leather bookbindings of the 18th and 19th centuries *Rhizopus nigricans*, Ehrenberg, *Mucor racemosus*, Fresenius, *Aspergillus niger*, van Tieghem (Fig. 1), *Aspergillus sp.*, *Fusarium sp.*, *Trichoderma viride*, (Persoon) Harz, *Penicillium claviforme*, Bainier and other *Penicillia* (Fig. 2) and *Streptomyces coelicolor* Waksman and Henrici were isolated, when applying the following methods: samples of leather were moistured with distilled water and placed both face and back to the surface of agar. 4 kinds of solid medium were used

agar with distilled water at pH = 5.0 and 7.5

agar with NH_4NO_3 at pH = 5.0

agar Czapek-Dox with glucose

and gravel with distilled water

Agar with distilled water and the gravel with distilled water were the most suitable to isolate leather-loving fungi, because these media supplied only moisture and food derived from leather. After the fungi were isolated attempts were made to find out a biocide which could kill the bookbinding leather-loving microorganisms affecting the leather.

4-chloro-3-cresol, *p*-nitrophenol, *o*-phenylphenol, their sodium salts and phenylmercury acetate were tested 30 years ago. Experiments were carried out using the method of poisoned agar medium (Fig. 3), directly on leather, leather coated with ethylcellulose lacquer as well as on leather dressing consisting of a mixture of lanolin, cedarwood oil, beeswax and hexane (Figs. 3-6). The activity of salicylanilide when applied to the coating of ethylcellulose lacquer has also been evaluated. In practice before using fungicide for protection purposes, leather bookbindings were disinfected and disinfected with a mixture of ethylene oxide and carbon dioxide (10:1). In case of leather cracking a dressing just mentioned and used by the British Museum was applied.

It is worth mentioning that the disinfection of leather objects of former Nazi camps in Oświęcim and Majdanek and in Ethnographical Museums have been carried out by us using 1-5% of ethyl alcohol solution of 4-chloro-3-cresol at the amount of 1 g on m^3 of leather objects. Exhibits of these museums were abundantly infected with pathogenic for leather and man fungi such as *Aspergillus fumigatus*, Fresenius, *Phialophora*, some species of *Alternaria*, *Chaetomium*, *Penicillium*, *Streptomyces* and others not identified. In case of very strongly in-

Microbiodeterioration of Library Materials

fectured exhibits by leather-loving and pathogenic for man microflora coming from nearly the whole of Europe we have used 2.5 g on m³ of 5% ethyl alcohol solution of 4-chloro-3-cresol. Proposed fungicide and bacteriostatic 4-chloro-3-cresol is not harmful to the human body and is the component of the formulation of disinfectant for personal hygiene purposes in medicine. Moreover it hasn't a deleterious effect on the environment.¹⁰

*4.6.2 Abstract**Decomposition of Leather by Microorganisms*

Leather writings and leather bookbindings are liable to disintegrate in the course of many years. From leather samples different leather-loving fungi and Streptomyces were isolated by using particularly two media: Agar with distilled water and gravel with distilled water.

Some fungicides to protect leather against microorganisms, as also ethylcellulose lacquer and leather dressing with fungicide were evaluated.

*4.6.2 Résumé**Décomposition du cuir par action microbienne.*

Les textes rédigés sur cuir et les livres reliés en cuir ont une tendance à la décomposition après de nombreuses années. Diverses moisissures et des streptomyces ayant une affinité pour le cuir ont été isolés à partir d'échantillons de cuir en utilisant en particulier deux substrats: Agar à l'eau distillée et "milieu spécial" à l'eau distillée. Quelques fongicides destinés à la protection du cuir contre l'action des microorganismes, tel que la laque à l'éthylcellulose et le produit d'entretien pour cuir à base de fongicide ont été essayés.

*4.6.2 Resümee**Zersetzung von Leder durch Mikroorganismen.*

Lederschriften und Lederbucheinbände neigen dazu, sich im Laufe vieler Jahre zu zersetzen. Aus Ledermustern wurden verschiedene von Leder lebenden Pilze und Streptomyces isoliert. Zu diesem Zweck wurden insbesondere zwei Medien verwendet: Agar mit destilliertem Wasser und Kies mit destilliertem Wasser. Hier wurden ebenfalls einige Fungizide, die Leder gegen Mikroorganismenbefall schützen, sowie Äthylzelluloselack und Lederdressing mit Fungizid beurteilt.

4.6.3 References

1. Bielaja, I. K.: *Methods of Strengthening the Damaged Leather of Old Bindings*. Restaurator 1 (1969): 93-104.
2. Block, S. S.: In Torgeson, D. C. (edit.) *Fungicides I* (1967): 379, Academic Press, New York.
3. Block, S. S.: In Lawrence, C. A. & Block, S. S. (eds.): *Disinfection, Sterilization and Preservation*. Lea and Febiger. Philadelphia 1968: 575.
4. Galloway, A. C. & Cooper, D. R.: *Fungicides for Treating Wet Blue Hides*. Journal of the Society of Leather Technology Chemists, 58 (1974): 67.

5. Haines, B. M.: *Leather*. Journal of Applied Chemistry and Biotechnology 25 (4 and 5) (1974): 294.
6. Hendry, M. F., Cooper, D. R., Woods, D. R.: *The Microbiology of Curing and Tanning Processes*. Part IV. The Laboratory Screening of Antiseptics. Journal of American Leather Chemists Association 66 (1971): 31-39.
7. Kowalik, R. & Czerwińska, E.: *Wybrane Zagadnienia Mikrobiologii Technicznej*. Podstawowe Problemy Współczesnej Techniki. Polska Akademia Nauk. Warszawa 1971.
8. Lucas, A. & Harris, J. R.: *Ancient Egyptian Materials and Industries*. E. Arnold Ltd. London 1962.
9. Pauli, O.: *Unbedenkliche Anstrichfungizide und Konservierungsmittel*. Farbe und Lack 77 (9) (1971): 888-890.
10. Pauli, O. & Franke, G. In Walters, A. H. & Hueck, van der Plas, E. H. (eds.) *Biodeterioration of Materials* vol. 2, Applied Science Publishing Ltd., London 1972: 52-60.
11. Reed, R.: *Ancient Skins, Parchments and Leathers*. Seminar Press. London and New York 1972.
12. Robbertse, P. J., Woods, D. R., Reay, A. H., Robb, F. T.: *Simple and Sensitive Procedure for Screening Collagenolytic Bacteria and the Isolation of Collagenase Mutants*. Journal of General Microbiology 106 (1978): 373-376.
13. Van Deren, J. M. & Weiss, E. F.: *Controlling Fungal Growth on Leather: Correlation of TCMTB Uptake and Duration of Mold Resistance*. Journal of American Leather Chemists Association 73 (1978): 448-507.
14. Werner, A. E.: *The Conservation of Leather, Bone and Ivory and Archival Materials In The Conservation of Cultural Property*. Unesco, Lausanne 1968.
15. Woods, D. R., Rawlings, D. E., Cooper, D. R., Galloway, A. C.: *Collagenolytic Activity of Hide Bacteria and Leather Decays*. Journal of Applied Bacteriology 36 (1973): 289-295.

Dr. Romuald Kowalik
Microbiological Laboratory
Institute of Industrial Organic Chemistry
03-236 Warsaw
Annopol 6
Poland

The Need for Detailed Watermark Research

by THOMAS L. GRAVELL

Although watermarks dating from 1500 to 1699 have been studied fairly extensively, little has been done to determine how long the paper on which those marks appear was available for use. Watermarks from this period which contain a date are rare. For example, in the extensive manuscript holdings of the Folger Shakespeare Library, fewer than ten dated watermarks have been found. It is possible to establish approximately when a sheet of paper was used if the same watermark can be found on a document which is dated. However, there are other means of establishing a frame-work for comparative dating of documents. These involve using the name or initials contained in the watermark. Names can often be located in local histories and in tax records thus establishing the date that the mill was in operation. Initials, on the other hand, present a different problem, for how can we be sure who used them or who they represented. This problem with initials might well be circumvented if, through the detailed examination of several archives, we could establish a timetable of the dates of use. Often the important task is to establish a time frame for a manuscript rather than to identify the particular papermaker or mill which produced the paper.

In recording the watermarks in the Folger manuscript collection I have noticed that several sets of the same initials keep reappearing in different years. The manuscripts that I have used are letters, business and official documents whose dates establish a time of use. There are a total of 369 different sets of initials from which I have selected 50 as examples here. The choices were made with two points in mind: there had to be at least four (4) or more examples of each watermarked item, and the examples had to fall within the period from 1500 to 1699. A numerical breakdown shows that 12 sets of initials occur on 4 items each, 23 on between 5 and 9 items, 10 on between 10 and 20 items, and the last 5 on between 21 to 86 items. The 86 items with the watermark "HG" were found on the "Newdigate News" letters for the years 1676 to 1686. The table below summarizes my findings:

Watermark Filigrane Wasserzeichen	Number of Items Nombre d'articles Anzahl	Time Span Période Zeitspanne	Devices Emblèmes Muster
AA	15	1578-1604	Pot
<u>A</u>			
GG	10	1589-1600	Pot
Ah	9	1589-1598	Pot
AN	4	1666-1679	Arms of Genoa
<u>C</u>			
AB	4	1649	Pot
CC	7	1618-1673	Hand, Pillars
DG	6	1587-1616	Crown
<u>D</u>			
IV	10	1605-1653	Pot
E	4	1543-1548	Shield
EB	5	1693-1698	Arms of London
EM	4	1593	Cross
F	4	1578-1597	Eagles, Pot
FL	8	1589-1600	Sphere
F ♣ E	6	1677	
G ♥ AR	6	1612-1622	Pillars
GB	27	1574-1689	Flag, Arms of Genoa, Pot
GD	10	1570-1697	Pillars, Pot
GF	6	1594-1693	Unicorns, Arms of London
GG	14	1670-1697	Pillars, Pot, Grapes
<u>G</u>			
LF	15	1678	Pot
<u>G</u>			
LM	5	1677-1678	Pot
<u>G</u>			
RO	4	1641-1650	Pot
HD	5	1696-1698	Lions in shield
HG	86	1676-1686	Post horn, Fleur-de-lis
<u>I</u>			
AV	5	1603-1642	Pot
IB	23	1549-1702	Hand, Pot
IG	4	1597-1631	Unicorns, Pot
II	4	1611-1676	Pot, Arms of Amsterdam
IM	8	1568-1694	Pot, Grapes, Crown
IP	6	1679-1692	Post horn, Arms of Amsterdam
<u>I</u>			
QQ	6	1584-1627	Pot
IR	4	1550-1579	Hand, Cross
IRO	9	1648-1678	Pot, Cardinal's hat

Watermark Filigrane Wasserzeichen	Number of Items Nombre d'articles Anzahl	Time Span Période Zeitspanne	Devices Emblèmes Muster
MC	4	1556-1638	Grapes
MD	8	1551-1602	Hand, Unicorn, Pot
NB	14	1553-1674	Pot
ND	5	1589-1598	Sphere
P	7	1554-1559	Flower
PB	15	1553-1609	Hand, Pot
<u>PD</u>			
B	21	1558-1630	Pot
PO	22	1543-1650	Pot, Post horn
<u>P</u>			
QQ	5	1597-1622	Pot
PL	7	1675	Post horn
RA	5	1552-1585	Hand, Pot
RB	14	1525-1631	Unicorn, Hand, Pot
RG	7	1559-1650	Hand, Pot, Post horn
<u>R</u>			
GG	4	1519-1603	Pot
RH	5	1551-1689	Crown, Hand, Pot
<u>RO</u>			
M	10	1551-1668	Hand, Pot, Arms of Genoa
W	4	1599-1614	Fleur-de-lis, Post horn

Although this listing is extremely limited, several things do emerge. For one thing, with additional recordings a definite time frame for availability of a particular watermarked sheet could be established. Secondly, it would be possible to trace the routes that paper trade took working from a listing of the places where the paper was used. While a listing of only four items has little meaning, if ten, or fifteen, or twenty examples of the same watermark could be found, a definite trend could be established and a comparative date arrived at.

A watermark found on the first Provost papers at Trinity College, Dublin, of a $\frac{C}{AB}$ dated 1623 falls within the 1649 range for the same watermark found at the Folger Library in Washington, D.C. (Fig. 1).

So does the "IG" in a pot dated 1597. (Fig. 2).

A letter signed *Katherine Paar*, dated 1546, in the John Boyd Thacher autograph collection at the Library of Congress has the "PB" watermark which on the list falls within the 1533-1609 period. (Fig. 3).

These sheets of paper, used by different persons in the same time period and now reposing in widely separated archives and manuscript collections, do, I

believe, demonstrate the value of a widespread, cooperative effort to record the dates of use.

The fact that some of the sheets with the same watermarks have widely spaced dates of use does not always mean that the paper remained unsold or unused. While this may be true in some instances, it is also true that papermills were handed down from father to son and even to grandsons. Such continuing ownership could be one explanation for why a certain set of initials will occur over a long time span. Furthermore, sometimes after mills changed hands the new owners continued to use the already established watermarks. Finally, master papermakers and journeymen often owned their own paper moulds which they used as they moved from mill to mill.

The same watermark can appear on different types of paper. In the early days papermaking materials and instruments were both costly and scarce. The cost of the mould alone guaranteed that it would be used to the fullest. By altering the amount and quality of the pulp in the vat papermakers could make many types of paper – writing, printing and even wrapping – with the same mould. The use of the same mould or pair of moulds would account for the appearance of the same watermark in printing and writing paper of the sixteenth and seventeenth centuries. The addition of sizing, or the pressing, bur-nishing and drying of the finished sheet all took place after the paper was made and would have little to no effect on a watermark already formed. Even news-papers of the eighteenth century were occasionally printed on watermarked paper.

One advantage of manuscripts in watermark research is that the manuscript is very often on a full sheet of paper and so shows both the watermark and countermark. The countermark is the more important of the two for dating, for many early papermakers or mill owners would use the same local mould maker. These mould makers used the same devices such as crowns, fleur-de-lis and post horns on their moulds. As a result, several different mills might have the same device as a watermark, but each would have a different countermark, consisting of a name or a set of initials. Only the largest mills could afford their own mould maker and few reached this size until the nineteenth century.

With the wide spread availability of both the Beta plate and the Dylux method for reproducing watermarks, it is now time to start compiling an archive of watermarks. While the works of Heawood, Churchill, Briquet and others are of immense value in supplying watermark information they reproduce only tracings and are, therefore, subject to error. The negatives obtained with a Beta plate and the Dylux prints are exact copies of the originals. Photographs made from them, if a millimeter scale is included, could be used to establish duplicate files in a number of archives. A joint effort by those research



Fig. 1

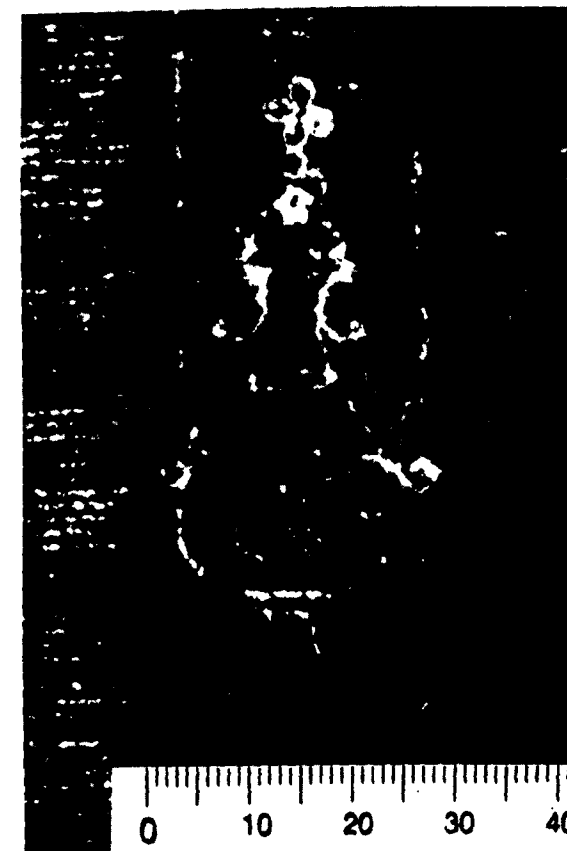


Fig. 2



Fig. 1. $\frac{C}{AB}$ pot, 1649 range.

Fig. 2. "IG" pot, 1597.

Fig. 3. "PB" hand, 1546.

libraries which already own Beta plates could produce an invaluable collection of watermarks. Photographs could be exchanged until all the participating institutions had a complete set.

In the last few years I have received a number of queries about particular watermarks. Some of the questions had easy answers. Others, much to my chagrin, required answers like "how long is a piece of string." The "how long" questions could have been answered correctly but only after a great amount of data had been gathered. If researchers would pool their findings in one central place or in a series of places, the "string" would be very short indeed.

ABSTRACTS

The Need for Detailed Watermark Research

Detailed research is needed so that comparative dates can be established for watermarks of the 1500 to 1699 period. A listing of watermark initials indicates the possibility of a time frame existing for their appearance in paper. Manuscripts on full sheets often show both the watermark and countermark whereas books do not. With the use of the Beta plate and Dylux methods a large archive of watermarks is possible.

Nécessité de travaux de recherche détaillés sur les filigranes

Des travaux de recherche détaillés s'avèrent nécessaires permettant de fixer des dates comparatives valables pour les filigranes de la période allant de 1500 à 1699. Un état détaillé des initiales en filigrane indique la possibilité d'existence d'une période d'apparition des filigranes sur le papier. Des manuscrits en feuillets, à l'encontre des livres, révèlent la présence simultanée de filigranes et de filigranes enfoncés. L'emploi des méthodes "Plaque Béta et Dylux" permet de constituer des archives importantes de filigranes.

Die Notwendigkeit einer ausführlichen Wasserzeichenforschung

Eine gründliche Forschung ist erforderlich, so dass für die Periode 1500 bis 1699 vergleichende Daten erstellt werden können. Durch eine Katalogisierung der Wasserzeichen-Initialien ergeben sich Hinweise darauf, dass es für deren Anwendung im Papier zeitlich abgegrenzte Rahmen gibt. Manuskripte auf ganzen Seiten weisen oft sowohl das Wasserzeichen als auch das Gegenzeichen auf, während dies bei Büchern nicht der Fall ist. Mittels der Beta-Platten- und der Dylux-Methode ist eine umfangreiche Sammlung von Wasserzeichen möglich.

Thomas L. Gravel
305 Mansion Road
Wilmington, DE 19804
U.S.A.

Restoration and Storage of Lead Artifacts

by GIUSEPPE GUIDA, MAURIZIO MARABELLI &
INGRID REINDELL

INTRODUCTION

This paper summarizes an experimental work on restoration and conservation of some lead objects, which, owing to the corrosion conservation processes and to the unfavourable storage conditions, were in an advanced stage of deterioration. The main factor of this deterioration – the electrochemical corrosion – attacked the objects and made them brittle. Therefore it was necessary first of all to carry out a conservation treatment and a subsequent research was planned for checking the best storage system.

Six objects were treated: five were Roman lead tesserae, belonging to the Altieri collection and coming from Kircheriano, preserved at the Numismatic Room of the Museo Nazionale Romano; the other was a papal seal of the 14th century, attached to a papal edict on parchment from the State Archives of Perugia.

Both the tesserae and the seal were almost totally covered by a layer of corrosion products, so that it was difficult, and in some cases quite impossible, to distinguish the underlying reliefs.

The corrosion products, partly powdery and partly granular and varying in colour (white-yellow-brown), were not only superficial but also penetrated the mass of the objects. These were very brittle, so that it would have been possible to inadvertently remove some particles, or even to break them. Therefore it was necessary to carry out an immediate restoration of the objects, in order to make the surface readable, to reinforce the corroded layers and to halt the corrosion process. The treatment to be applied had obviously to guarantee a minimal loss of material and to be performed under controlled conditions.

Some experiences have been carried out in recent years on the causes of lead corrosion,^{1, 2, 3, 4} on the method for preventing it^{2, 3, 4} and on the restoration processes.^{1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15}

Many methods are available for removing corrosion products: among the most effective, in addition to mechanical cleaning, chemical cleaning with acetic acid,^{1, 13} with various sodium salts of E.D.T.A (ethylenediaminetetraacetic acid),¹² with diluted hydrochloric acid and ammonium acetate,¹⁴ with ion-exchange resins,¹¹ and, lastly, ultrasonics.^{8, 9, 10} None of the above mentioned

methods consolidates the structure. For consolidation it is better to carry out an electrolytic reduction,^{5, 6, 7} possibly utilizing the apparatus suggested by Organ.¹⁵

Electrolytic reduction

Electrolytic method is widely used: oxidized lead is entirely reduced to metal lead, due to reduction at the cathode, $\text{Pb}^{++} + 2\text{e} \rightarrow \text{Pb}^0$. This technique can be performed in standard and controlled conditions, with a minimal loss of material; it is also economically advantageous, for it makes use of very simple equipment, a disadvantage being, however, the long time normally required for the electrolytic process. The electrolytic treatment may be carried out in acid or alkaline solution at a low current density. The solution adopted in the present work was acid (10% sulphuric acid), the current density 100–200 mA/dm², and the voltage 2–3 volts. If a higher current density (300 mA/dm²) is used the evolution of hydrogen gas bubbles may determine a reduced porous structure, and may also remove some particles of corrosion products.

The object is the cathode, while the anode is composed of two thin (0.4 mm) lead plates, in front of each side of the object at a distance of 8 mm.

The scheme of the electrolytic cell is shown in Figure 1.

Before electrolytic reduction, it was possible by X-ray diffraction to detect

CATHODE ANODE

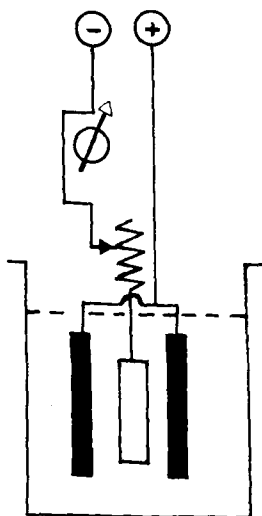


Figure 1. Scheme of the electrolytic cell.

Figure 1. Schéma de montage de la cellule électrolytique.

Abb. 1. Schematische Darstellung der Elektrolytzelle.

hydrocerussite [basic lead carbonate, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] on all the objects. The formation of corrosion products, because of the deterioration processes, is also often dependent on storage conditions. Volatile organic acids (mostly acetic acid from some types of wood) and humidity are the main factors of corrosion.

Restoration of the tesserae and the seal

Both the tesserae and the seal were washed with hot acetone and trichloroethane in order to eliminate any grease or waxy products. After drying in a thermostatic stove at 40°C each object was weighed (weighing before and after reduction is necessary to check any possible loss of material) and was then connected with the negative pole of a direct current generator by means of a platinum wire.

At the end of the electrolytic process, the objects were repeatedly briefly washed with boiled distilled water to remove H_2SO_4 and soluble salts; the treatment was repeated until a neutral pH was attained. Then the objects were dried by dipping in acetone and trichloroethane successively, and finally were gently brushed to remove any very thin lead sulphate layer formed on the surface.

Table 1 shows the weight losses per unit area after reduction and after brushing and the experimental parameters.

Figures 2 and 3 show photographs of the seal before and after restoration.

Table 1. Data on reduction process and weight losses of the tesserae and of the seal.

Table 1. Résultats du traitement de réduction et des pertes de poids des tessères et du sceau.

Tabelle 1. Daten des Reduktionsprozesses und der Gewichtsverluste der Tafeln und des Siegels.

Type of object	Total weight loss after reduction mg	Total weight loss after reduction and brushing mg	Total surface cm ²	Weight loss per unit area after reduction mg/cm ²	Weight loss per unit area after reduction and brushing mg/cm ²	V volts	I mA	Reduction time days
Tesserae 1	12.5	131.0	7	1.8	18.7	2–3	7	8
Tesserae 2	11.0	107.2	7	1.6	15.3	–	7	9
Tesserae 3	36.9	170.2	7	5.3	24.3	–	7	10
Tesserae 4	83.1	202.8	7	11.9	29.0	–	7	7
Tesserae 5	–	–	7	–	–	–	7	7
Seal	103.8	1052.4	24	42.4	43.8	–	24	14



Figure 2a. Seal (recto) before restoration.

Figure 2a. Recto du sceau avant restauration.

Abb. 2a. Siegel ("recto") vor der Restaurierung.

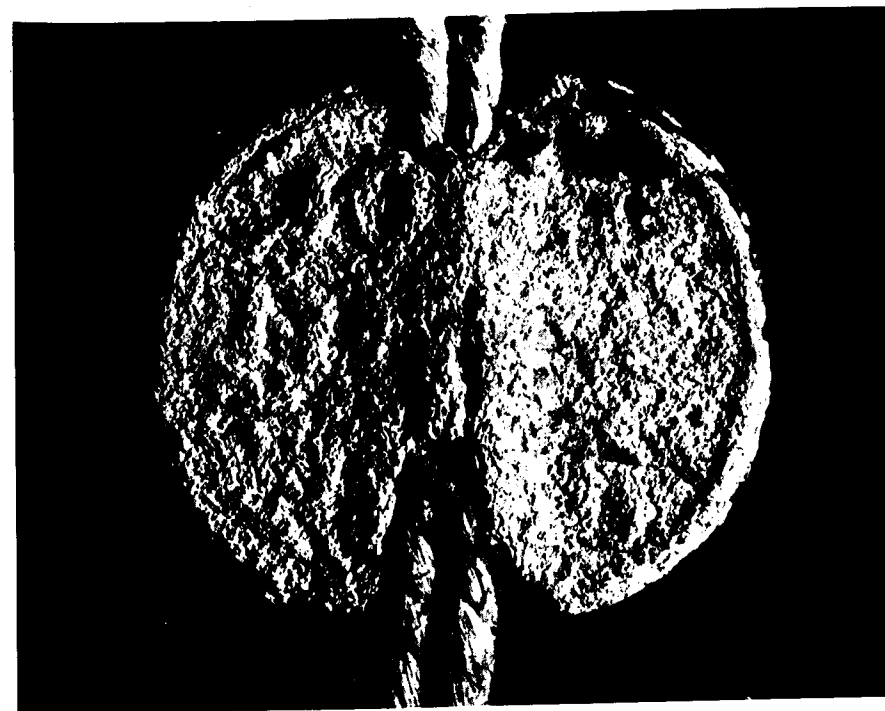


Figure 3a. Seal (verso) before restoration.

Figure 3a. Verso du sceau avant restauration.

Abb. 3a. Siegel ("verso") vor der Restaurierung.



Figure 2b. Seal (recto) after restoration.

Figure 2b. Recto du sceau après restauration.

Abb. 2b. Siegel ("recto") nach der Restaurierung.

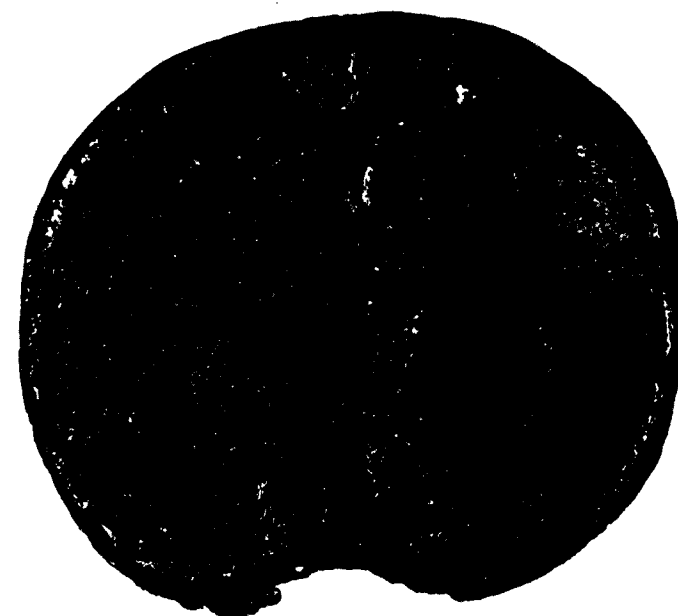


Figure 3b. Seal (verso) after restoration.

Figure 3b. Verso du sceau après restauration.

Abb. 3a. Siegel ("verso") nach der Restaurierung.

Provisions for storage

A further problem was to define a suitable method for storing the tesserae and the seal so as to minimize the risk of a new corrosion. This means that the objects ought to be stored at low relative humidity in suitable containers, which must be impermeable to moisture and acid vapours. These containers must obviously be easy to handle, transparent and suitable for storage in a narrow space. It was thus decided to check the water vapour permeability of some plastic films which, heat-sealed, might contain the objects and insulate them from the external environment.

Three different materials were chosen: a polyethylene film, 50 μm thick, manufactured by "Eurcellofan," a bioriented Moplefan film, 37 μm thick (a polypropylene film coated on both sides with a thermoplastic lacquer), and finally, a non-oriented Moplefan polypropylene film, 78 μm thick, both manufactured by Montedison.

The following procedure was adopted for checking the three films: three groups of four glass containers (h 6 cm and $\varnothing$ 3.5 cm) were filled with Merck silica gel, stove dried at 110°C, and each group was respectively closed with one of the three films. After sealing them with rubber rings, the containers were weighed and put into a glass box containing a saturated solution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, which ensured 80% R.H. at 30°C. The box was placed in a climatic chamber regulated at 80% R.H., 30°C. The cover of the glass box had a hole that allowed an air exchange with the inside of the chamber.

The moisture absorption was checked for twenty days, weighing the containers daily for the first ten days, and then on the fifteenth and twentieth day. From the weight increase it was possible to calculate, by means of the following

Table 2. W.V. Permeability values of the three films at different times.

Table 2. Vapeur d'eau. Valeurs de la perméabilité de trois films en fonctions du temps.

Tabelle 2. Wasserdampf-Durchdringbarkeitswerte der drei Folien zu verschiedenen Zeiten.

Type of film	Days	2	3	4	5	6	7	8	9	10	15	20
Polyethylene		21.4	51.0	80.9	108.4	164.0	190.5	222.4	252.0	279.9	394.5	505.5
Bioriented Moplefan		20.9	49.0	72.9	99.4	155.0	175.0	216.5	251.8	324.2	381.8	486.3
Non-oriented Moplefan		56.4	159.8	220.3	274.6	395.0	462.5	531.8	592.5	639.4	870.9	1062.0

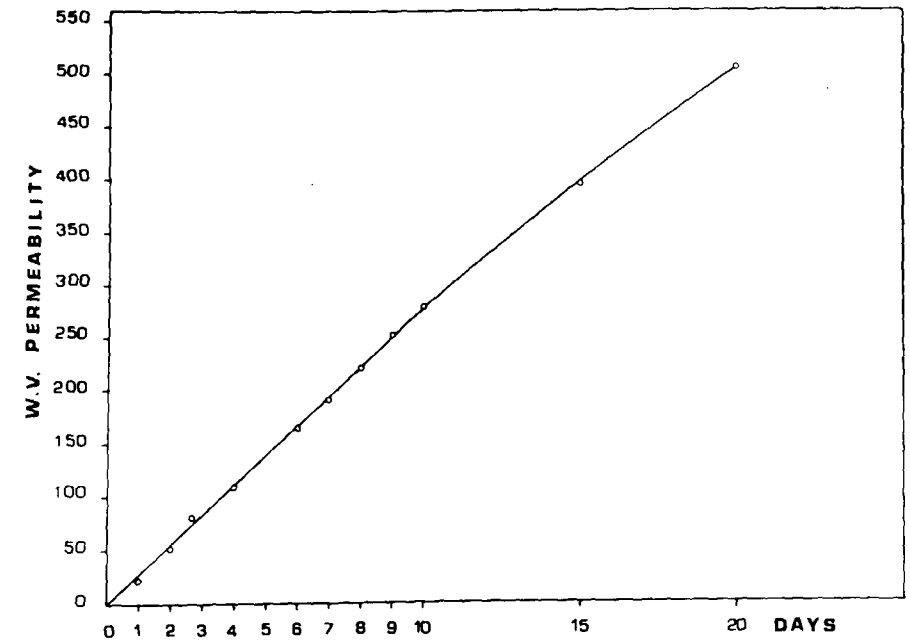


Figure 4. W.V. Permeability for polyethylene.

Figure 4. Vapeur d'eau. Perméabilité du polyéthylène.

Abb. 4. Wasserdampfdurchdringbarkeit für Polyäthylen.

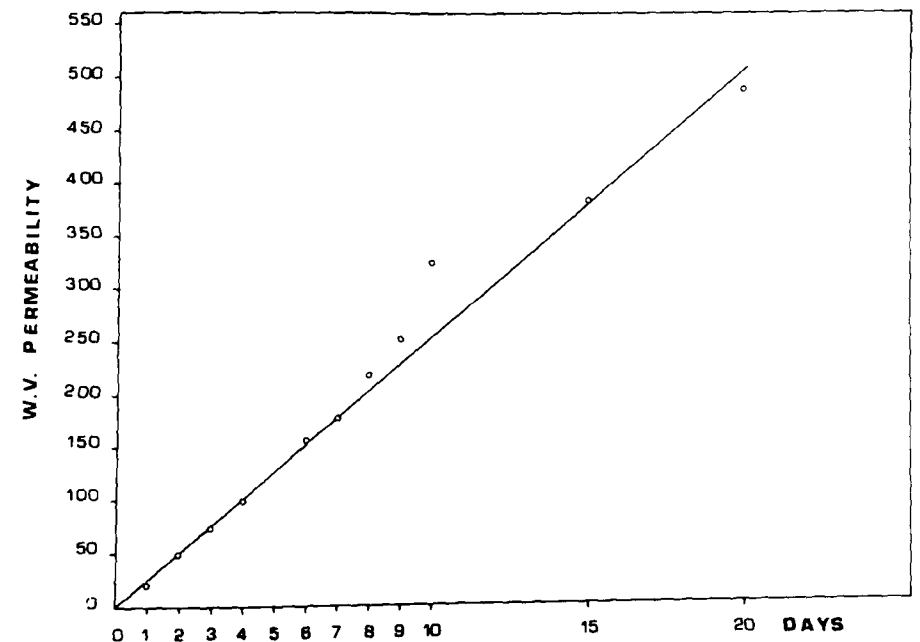


Figure 5. W.V. Permeability for bioriented Moplefan.

Figure 5. Vapeur d'eau. Perméabilité du Moplefan biorienté.

Abb. 5. Wasserdampfdurchdringbarkeit für biorientiertes Moplefan.

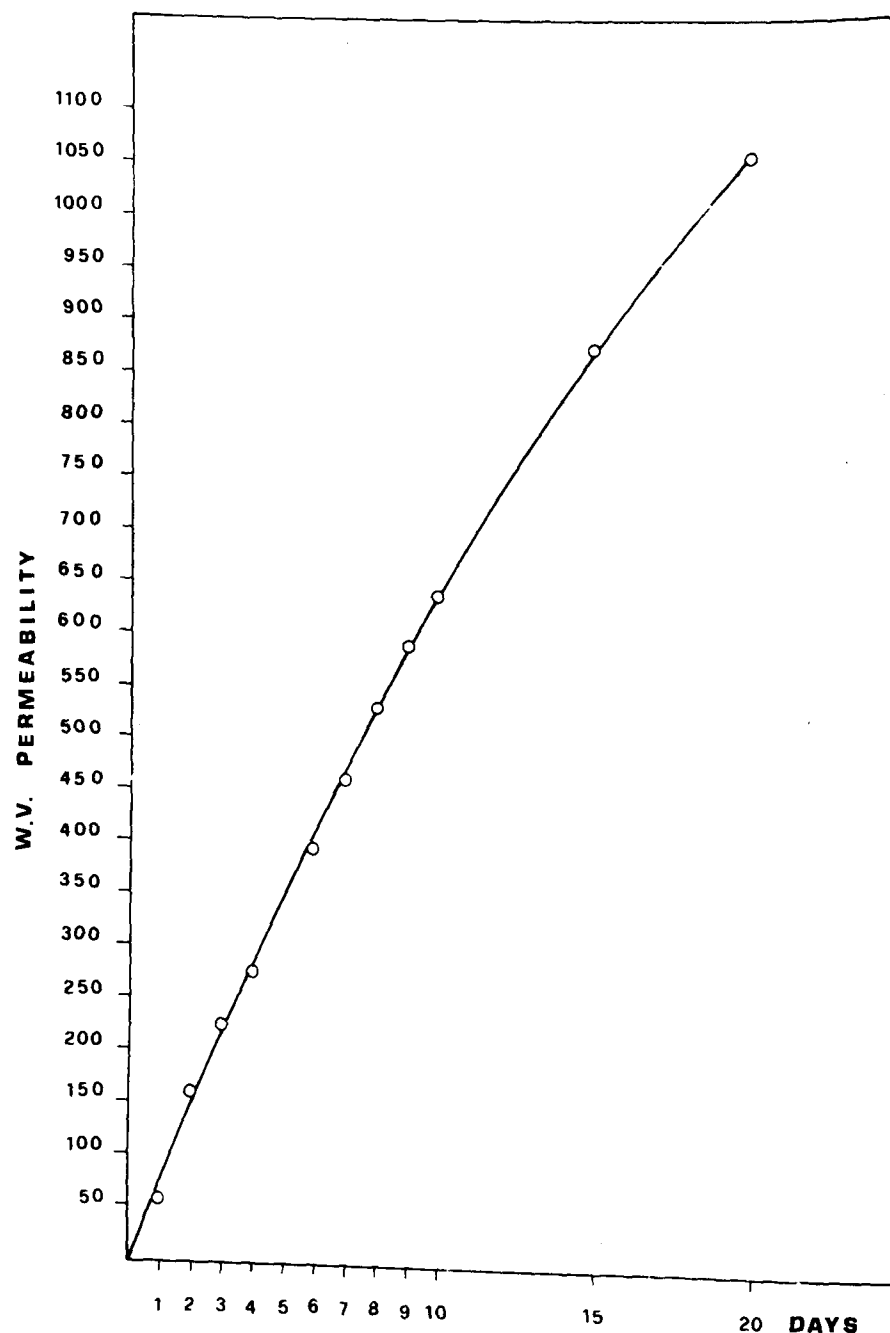


Figure 6. W.V. Permeability for non-oriented Moplefan.

Figure 6. Vapeur d'eau. Perméabilité du Moplefan anisotrope.

Abb. 6. Wasserdampfdurchdringbarkeit für nicht-orientiertes Moplefan.

formula, the water-vapour permeability (A) of each film at different times, referred to a standard thickness of 25 μm , an area of 1 m^2 and a surrounding atmosphere of 80% R.H. and 30°C:

$$A = \frac{\Delta p \cdot s \cdot 10^4}{a \cdot 25}$$

where:

Δp : weight difference in grams;

a: film area in cm^2 ;

s: film thickness in μm ;

25: factor referring back to the "standard" 25 μm thickness;

10^4 : factor referring to the "standard" 1 m^2 area.

The permeability values, thus calculated, and reported in Table 2, were plotted as a function of time (Figures 4, 5, 6).

From the diagrams, one can obtain the permeability coefficient of the three films which corresponds to the slope of the straight-line part of the diagrams. The coefficient values are: 27.7 for polyethylene, 25.0 for bioriented Moplefan and 67.0 for non-oriented Moplefan. On the basis of these values and on account of the handling and resistance properties of the three films, polyethylene is the most suitable material, for it has a sufficiently low permeability coefficient, it is reasonably flexible and can be easily heat sealed.

SUMMARIES

Restoration and Storage of Lead Artifacts

Reference is briefly made in this work to the main methods for restoration of lead objects. The application of the electrolytic technique is particularly stressed and this method was adopted for restoring some lead tesserae and a lead seal. The result of a test on some thermoplastic films for storage is also reported.

Restauration et stockage d'objets en plomb

Les principales méthodes de restauration d'objets en plomb font l'objet d'une mention brève. L'application d'une technique électrolytique est particulièrement indiquée; cette méthode a été adoptée pour la restauration de diverses tessères et d'un sceau en plomb. Le résultat de l'influence de divers films thermoplastiques sur l'entreposage/le stockage est aussi mentionné.

*Restoration and Storage of Lead Artifacts**Restaurierung und Lagerung von Gegenständen aus Blei*

Die vorliegende Veröffentlichung beschäftigt sich kurz mit den wichtigsten Methoden, die bei der Restaurierung von Gegenständen aus Blei Anwendung finden. Besonders hervorgehoben wird die Anwendung des Elektrolytverfahrens. Diese Methode wurde bei der Restauierung von einigen Bleitafeln und einem Bleisiegel benutzt. Daneben wird auch das Ergebnis aus einem Test mit thermoplastischen Folien, die zur Lagerung verwendet werden, wiedergegeben.

ACKNOWLEDGEMENTS

Many thanks to Dr. Silvana Balbi De Caro, Director of the Gabinetto Numismatico of the Museo Nazionale Romano and to Dr. Ermanno Ciocca, Director of the Archivio di Stato of Perugia, for the loan of the objects.

Many thanks also to Mario Micheli for his help in the restoration process.

The work was carried out in the chemical laboratory of Istituto Centrale del Restauro, under the guidance of Dr. M. Marabelli.

REFERENCES

1. Blakshaw, S. M., Daniels, V. D.: "Selecting safe materials for use in display and storage of antiquities" in *Atti ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978*, paper 78/23/2.
2. Evans, U. R.: *"The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications"*. E. Arnold, London, 1961, pp. 103-105.
3. Stambolov, T.: *"The Corrosion and Conservation of Metallic Antiquities and Works of Arts"*. Central Research Laboratory of Objects of Art and Science, Amsterdam, (w.d.).
4. Organ, R. M.: "The current status of the treatment of corroded metal artifacts" in *"Corrosion and Metal Artifacts"*, NBS Special Publication 479, 1977, pp. 107-142.
5. Marabelli, M., Cigna, R.: "Tecnica di restauro di due medaglie in piombo del Museo Civico di Trieste", scheda I.C.R. 456, 4/4/1972.
6. Organ, R. M.: "The consolidation of fragile metallic objects" in *"Recent Advances in Conservation"*, Thomson, G., London, 1963, pp. 128-134.
7. Organ, R. M.: "The method for lead and lead alloys", *ICOM Inquiry into Procedures for Electrolytic and Electro-Chemical Treatment of Mineralized Metal Antiquities - Part III*, 1969, pp. 1-15.
8. Bichaton, N.: "Methode scientifique et pratique pour le traitement des monnaies en plomb" in *Atti della XLIX riunione S.I.P.S.*, Settembre 1967, S.I.P.S., II, 1063-1064 (1968).
9. Spier, R. F. G.: "Ultrasonic cleaning of artifacts: a preliminary consideration", *American Antiquities*, XXVI, 3, 410-414 (1961).
10. Muehlealer, B.: "Ultrasuoni per la pulitura di reperti degli scavi archeologici", *Neue Zuercher Zeitung*, 19, 2, 1964 (w.p.).
11. Organ, R. M.: "Use of ion-exchange resin in the treatment of lead objects", *Museum Journal*, LIII, 49-52 (1953).
12. Kuhn, H.: "Neue Reinigungsmethode für korrodierte Bleigegegenstände", *Museumskunde*, 29, 156-161 (1960).
13. Lane, H.: "The reduction of lead", in *"Conservation in Archeology and the Applied Arts"*, *Atti I.I.C.*, *Stockholm Congress 1975*, preprints pp. 215-217.
14. Caley, E. R.: "Coatings and incrustation on lead objects from the Agora and the method used for their removal", *Studies in Conservation*, II, 49-54, 1955.
15. Organ, R. M.: *"Design for Scientific Conservation of Antiquities"*, London, Butterworths, 1968.

Giuseppe Guida: Centro di Fotoriproduzione, Legatoria e Restauro degli Archivi di Stato. Via Costanza Baudana 14, 00153 ROMA.

Maurizio Marabelli: Istituto Centrale del Restauro. Piazza San Francesco di Paola 9, 00100 ROMA.

Ingrid Reindell: Soprintendenza Archeologica di Roma. Museo Nazionale Romano, Medagliere. Piazza delle Finanze 1, 00100 ROMA.

The Committee on Production Guidelines
for
Book Longevity

Interim Report on Book Paper,
April 1981

In the past few years there has been increasing awareness that millions of books and other documents all over the world are disintegrating. We are in danger of losing more than a century of the human record – since the early 19th century when paper manufacturers began the widespread use of processes that left acidic residues in paper. Such residues in the presence of light, heat, moisture, and air hasten the process of deterioration of the cellulose fiber, thus weakening the paper. For example, over six million volumes in the Library of Congress are now so brittle that their survival is threatened. Much effort has been expended, with very modest success, to devise economical ways of preserving these books. Much more needs to be done.

Our concern here is not with preserving the books of the past, but rather those of the future. Books containing the acidic seeds of their own destruction continue to be produced by the millions, storing up problems for the future, failing to provide a permanent record of our own times.

Our Committee on Production Guidelines for Book Longevity was formed by the Council on Library Resources, with help from the A. W. Mellon Foundation, to seek ways to encourage the production of publications that will last, especially books. We recognize that this is a herculean task. It would be useless for us to ignore economic forces; recommendations for improvement must stand the harsh test of the marketplace. Nevertheless, as we shall explain, we are optimistic. Some technological factors are working for us. Much can be accomplished through more awareness, through good will, and through cooperation, without adding substantially or even at all to the cost of many books.

Who's to blame? The public has awarded the largest share of blame for our present situation to the paper manufacturers, but are they at fault? Have they not, with enormous investment, met the demand of publishers for low-cost book paper, and has not this availability led to the huge expansion of reading? Until thirty years ago paper mills were not able to produce acid-free book paper at competitive prices, but now they can. Others say that poor paper standards are

the fault of the publishers, but publishers have met the need of the public for low-priced books, and until recently few complained about paper permanence. The problem has been recognized since the 1950's, and even today librarians, who worry about prices and about preservation of old books, seldom ask about the structural quality of what they buy. Permanence was not a conscious part of book production decision-making. The problem is big and complicated; no one group is to blame, and exigencies of the day tend to push the problem aside to be dealt with by the librarians and the readers of the future.

What is being done? Actually, without a major effort, the situation is improving gradually. For reasons having nothing to do with permanence, the processes for making acid-free book paper were developed in the 1940's. Although the problem of disintegrating books was recognized much earlier, not until the Barrow reports of 25 years ago did publishers pay any attention. At that time, in response to a brief outcry from librarians, several publishers announced that henceforth they would use only acid-free paper. But lack of commitment and shortages in supply caused the practice to be abandoned except by a few publishers. Recently both economic forces and the anti-pollution laws have increased interest in acid-free paper production. The trend is slow because the necessary technological changes are expensive (a large new paper machine costs more than \$ 1,000,000), but it appears that in another decade the effects may be substantial. We estimate that in 1980 about 25% of paper manufactured in America for use in book production was acid-free (about 225,000 tons of a total of 840,000). This percentage will probably increase by 1990. Can we hasten this transition? In the long term production responds to demand.

It should be recognized, however, that there are some strong opposing forces, especially the increasing use of groundwood, primarily in mass-market paperbacks and some textbooks. This use may be extended to other books too. Groundwood in any amount causes paper to deteriorate quickly. It is our hope that the increasing use of acid-free paper will offset the use of groundwood papers for books that need preserving. There is more groundwood paper, but there is also more acid-free paper.

What ought to be done? Should all book production, to say nothing of all other publications, be produced on "permanent" paper? That seems absurd. Much printed matter is made to be read and thrown away – newspapers, magazines, paperbacks. If they could be made permanent at no extra cost, no one would object, but it hardly seems reasonable to insist that they be manufactured to last for centuries. To the extent that they are wanted, other ways will have to be found to preserve them, probably mainly by microphotography. Much the same could be said of many books, though with hardbound books it becomes

more difficult to make distinctions. Even the most ephemeral popular books (like magazines and newspapers) are part of the record of our civilization and will be of interest to future generations. Still, distinctions can be made. Many books – especially scientific and scholarly books and serious works of fiction and nonfiction – are culturally valuable and must be preserved in some form.

At a recent meeting of librarians, publishers, and paper manufacturers it was suggested that the following categories of books ought especially to be printed on acid-free paper: *primary printed sources, important works of fiction and nonfiction, collected editions, bibliographies, guides to collections, yearbooks, gazetteers, scholarly periodicals and monographs, dictionaries, encyclopedias, and other reference books.*

With some trepidation it was suggested that the following categories need not be on acid-free paper: *Workbooks, textbooks, anthologies, vanity publications, athletic and political hagiography, popularizations in all fields, novelizations of films, formula novels, and most paperbacks.*

These lists cannot be definitive, but they can indicate directions. Ultimately publishers will have to make judgments. *The aims of our committee would be largely realized if publishers would be more aware of the need for "permanence" and would make thoughtful decisions about the paper used to print their books.* Publishers are proud of their books; they have the knowledge to make such judgments. They should remember, too, that not only libraries want "permanent" books. Book lovers of all kinds have a right to expect, when they buy an expensive art book or children's book or novel, that it will not disintegrate.

Cost. Acid-free paper need not be more expensive than acidic paper of the quality normally used in hardbound books.

Availability. The paper industry is huge; only a little over 1% of its total production is book publishing paper. Hence the book industry can have very little influence on the paper industry as a whole. Moreover, only a portion of book paper is used for hardbound books; we have already acknowledged that most paperbacks are by definition ephemeral. So, in seeking paper that will last we are concerned with a relatively small amount of production which can be supplied perhaps by fewer than ten companies. Publishers should use present acid-free production wisely, and we need to encourage the development of more acid-free mills. In recent years the demand for paper has risen, and book paper has sometimes been in short supply. In such conditions publishers will use what they can get. The supply in the next five years promises to be better.

Recommendations. Table 1 supplies information on the products of manufacturers producing acid-free paper. We offer guidelines that we think are desirable and economically reasonable, and we encourage publishers who follow the guidelines to make an appropriate statement to appear just below the copyright line. We suggest, for example:

The Committee on Production Guidelines for Book Longevity

The paper in this book meets the guidelines for permanence and durability of the Committee on Production Guidelines for Book Longevity of the Council on Library Resources.

Identification of acid-free books is important because book-buyers, especially librarians, need to know which books may require special care in the future or special storage conditions now. Libraries spend millions on preservation; often it is necessary to microfilm books to preserve their contents. To the extent that acid-free books are identified, these procedures will be less costly. Funds saved could be used to enlarge collections.

We encourage libraries to make their needs heard, especially to those publishers producing books that are purchased mainly by libraries, and also to general publishers. The library market is significant to every hardback book publisher. The American Library Association should encourage publishers to produce long-lasting books.

The U.S. Government is the largest publisher in the United States, and nearly all of its productions are on highly acidic paper. We encourage libraries to make their voices heard to the Joint Committee on Printing and to other government agencies issuing documentary publications of long-range importance. The American Library Association, the Association of Research Libraries, and other such groups should offer their services in helping to determine which categories of publications should be issued in permanent form.

Durability. Until now we have spoken only of chemical disintegration. Books also fall apart for other reasons. Book papers need not only "permanence" but "durability," the ability to withstand folding and tearing. Without going into detail here, we shall recommend guidelines for minimum folding and tearing qualities. In a later report we shall discuss binding materials, which are obviously important too. But here we have focussed attention only on the inside of a book, essentially its paper, because if that disintegrates a long-lasting binding is superfluous.

Production realities. Publishers do not usually buy paper for an individual title. They buy paper by the carload or in minimum quantities of perhaps 10,000 pounds, in standard sizes, for use in a variety of books as needed. The production of *groups of books*, all in the same trim size and with identical paper, will be arranged for economy in printing and binding. Under these conditions a publisher cannot usually choose a particular sheet for a particular book. He carries a stock of several different sheets in a few different sizes and makes his choice for each book from among these. *We urge publishers and especially their production managers, to stock at least some acid-free sheets for use on appropriate groups of books.*

Mills. The largest mills routinely producing acid-free paper at competitive

prices are Warren, Glatfelter, and (for lightweight paper) Olin. There are also a number of smaller mills (no mill is small) producing good acid-free sheets, often specialty sheets for art books and the like. Table 1 in the Appendix lists acid-free mills and some of the sheets they produce. Publishers are urged to refer to this table when purchasing paper.

APPENDIX

Guidelines. Although there are unresolved technical arguments about the validity of artificial aging tests, everyone agrees that acid causes paper to disintegrate. A pH of 7 is neutral¹; a higher pH is alkaline while a lower pH is acidic. A pH slightly higher than 7 is desirable because the pH of paper tends to become lower and more acidic over time due to chemical processes. Papers containing groundwood should be avoided entirely since groundwood deteriorates rapidly. Other characteristics of paper (opacity, printability, flexibility, etc.) may be affected by acid content, but we are confident that for any publication requiring permanence a suitable sheet can be found, without excessive cost, within the following guidelines²:

- Minimum pH of 7.5 (cold extraction, Tappi T-435)
- Minimum cross-direction folding endurance of 30 double folds at 1 kg tension (25 replicates, Tappi T-511)
- Minimum average machine direction tear resistance: (Elmendorf, 10 replicates, 8-ply tears, Tappi T-414) of 70 grams
- Minimum alkaline reserve (calcium or magnesium carbonate or both) of 2% based on oven dry weight

This standard applies specifically to uncoated 60 lb. paper (basis 25 × 38/60) or 90 gm./m².

The paper should be made of cotton or fully bleached wood pulp (or a mixture) and should include no unbleached wood pulp or groundwood.

No acid or chloride printing inks should be used.

Most books are printed on uncoated paper. Regardless of the weight, the pH factor should be maintained. For a given quality of papermaking materials, lower weight will mean less resistance to tearing and less endurance in folding. Depending on expected use, reduced folding and tearing characteristics may be tolerable.

The question of coated paper is not treated separately in this report. Modern coatings in general have a helpful effect on permanence, but pH standards should nevertheless be maintained. Fold and tear-test guidelines as given above apply to uncoated paper only.

Table 1.

Publishing Paper Table – Acid-Free Grades¹

1. Grades for General Publishing

Table 1. Table des papiers d'édition – qualités exemptes d'acidité

1. Qualités pour publication d'ordre général

Tabelle 1. Papiertabelle der Verlage – Säurefreie Qualitäten

1. Qualitäten für allgemeine Veröffentlichungen

Paper manufacturer and location	Type of Paper	Shades	Available Surfaces
S. D. Warren Div., Scott Paper Co. Westbrook, Me. Muskegon, Mich.	uncoated	white cream	antique eggshell machine finish
	coated	white cream*	gloss dull
	coated	white	matte
P. H. Glatfelter Co. Spring Grove, Pa. Neenah, Wis.	uncoated	white cream	antique eggshell machine finish
	coated	white	gloss matte
Finch Pruyn & Co. Glens Falls, N.Y.	uncoated	white cream	special order only
Allied Paper Mills Div., SCM Corp. Kalamazoo, Mich.	uncoated lightweight	white cream	special order only
Olin Corporation Fine Paper and Film Div. Pisgah Forest, N.C.	uncoated lightweight	white natural	machine finish supercalendered
Miami Paper Co. West Carrollton, Ohio	uncoated	white cream	antique eggshell
	film coated	white	matte
Consolidated Papers, Inc. Wisconsin Rapids, Wis.	coated	white	gloss dull matte

* Available certain items only.

2. Grades for Special Purpose Publishing
(regularly made or inventoried)**2. Qualité de papiers pour éditions spéciales
(production normale ou répertoriée)2. Papierqualitäten für spezielle Publikationen
(werden regelmässig hergestellt oder auf Lager geführt)

Curtis Paper Company Newark, Delaware	uncoated	white natural	antique
Howard Paper Company Dayton, Ohio	uncoated	white natural	antique
Mohawk Paper Mills Cohoes, N.Y.	uncoated	white soft white ivory	eggshell
Monadnock Paper Mills Bennington, New Hampshire	uncoated	white natural	antique eggshell smooth

** Generally heavier weights, and made on smaller, slower papermaking equipment; suitable for specialized uses, but not generally economically feasible for commercial publishing.

1. The above is for informational purposes only, and is not to be considered an endorsement or recommendation.

Grades of paper or their makers listed in this table are those ordinarily for trade, text, reference or scholarly book publishing. No attempt has been made to include papers permanent in nature ordinarily used for other purposes (e.g. record keeping) but unsuitable for book publishing use.

Only those paper manufacturers have been listed who make neutral or alkaline grades as part of a regular product line. Such papers are often available on special order, especially in the case of those suitable for special purpose publishing.

The paper industry continues to evolve in its use of raw materials and processes, and additions to this table, especially in the face of increased demand, are possible.

FOOTNOTES

1. pH is a symbol denoting the negative logarithm of the hydrogen ion concentration, in grams per liter, of a solution; it expresses relative alkalinity and acidity. The concentration of the free hydrogen ions is expressed as an exponent, so that pH 4 is ten times more acidic than pH 5 and one hundred times more acidic than pH 6.
2. These guidelines are adapted and simplified from the standards set by the National Historical Publications and Records Commission, the Library of Congress, and from the ASTM/ANSI Standard Specification for Bond and Ledger Papers for Permanent Records.

DEFINITIONS

antique – the roughest surface of uncoated paper normally used in publishing, consequently the bulkiest paper per inch.

coated – paper to whose surface a coating of clay, calcium carbonate or other pigment or mixture of pigments has been added to provide a smoother base for printing.

Dull – coated paper whose surface has been left unpolished or has been otherwise treated to provide a non-reflective appearance for better readability or contrast with gloss inks.

Gloss – coated paper that has been supercalendered (polished) for smoothness. Shiny in appearance.

Matte – a type of coated paper carrying less surface coat weight than dull. Has a non-reflective surface, neither as smooth nor as refined as dull coated.

Color – hue or shade, as distinguished from brightness. White, for this purpose, means that the underlying shade of the paper is toward the cold, or blue, end of the spectrum. Paper made with a yellow cast and whose underlying shade is toward the warm, or red, end of the spectrum is variously called natural or (darker) cream, or in some cases, ivory.

eggshell – not as rough as antique and less bulky, but still possessing a noticeable degree of texture.

Groundwood – pulp produced by mechanically defibering wood without chemical cooking. The resulting high-yield pulp contains many impurities, notably lignin, which deteriorates markedly on exposure to light and air.

lightweight – a loose term describing paper lighter than 45 lb. (25 × 38 basis) or 67 grams per square meter. Heavily opacified; used for reference books, dictionaries, Bible, etc. Sometimes called “Bible paper” or “thin paper”.

machine finish – a “natural” finish as paper comes off the paper machine with only a modest attempt at compacting the web at the machine calender. Smooth to the touch.

supercalendered – paper that has been run through a series of polishing rolls (supercalender) off the paper machine. Very smooth and slick to the touch. Gloss coated paper generally has been supercalendered, and plain paper may be treated in this way.

uncoated – paper whose surface is not covered by clay or other material; also called “plain” paper.

The Committee on Production Guidelines for Book Longevity of
the Council on Library Resources

Herbert S. Bailey, Jr., Chairman (Princeton University Press)
Frank G. Burke (National Historical Publications and Records Commission)
Warren J. Haas (Council on Library Resources)
Peter Mollman (Random House, Inc.)
Leonard D. Schlosser (Lindenmeyer Paper Corporation)
David H. Stam (New York Public Library)
R. Gay Walker (Yale University Library)

Warren J. Haas
Council on Library Resources
One Dupont Circle
Washington, DC 20036
USA

RESTAURATOR

International Journal for the Preservation
of Library and Archival Material

Volume 4 · 1980

EDITOR:

POUL A. CHRISTIANSEN

University Library: Scientific and Medical Dept.
DK-2200 Copenhagen N, Denmark

ASSOCIATE EDITORS:

N. S. BAER, New York, N.Y.

GÜNTER BRANNAHL, Göttingen, FR Germany

RICHARD D. SMITH, Park Forest, Illinois

MUNKSGAARD · COPENHAGEN

Editorial Notice

RESTAURATOR. *International Journal for the Preservation of Library and Archival Material*, will bring original papers on the subjects mentioned in the titles (including etchings and engravings), as well as reviews and news of interest to scientists, conservators, archivists, and librarians.

Contributions will be accepted in English, French, or German. Abstracts and figure legends will be printed in these languages. Contributors not writing in their mother tongue are particularly asked to have their manuscripts checked for linguistic and stylistic errors.

Manuscripts should be original typescripts (not carbon copies), in double spacing and on one side only of the paper. They must be carefully revised, as alterations in print are expensive. The paper used must be non-absorbent. Author's name should be accompanied by the title, position and working place of the author.

An abstract of no more than 200 words should be sent with the manuscript. The abstract should be in the same language as the article. The publisher will provide translation into the two other languages, of the abstract and the figure legends.

All graphs, drawings, or photographs are to be referred to as figures (abbr. Fig.) and should be numbered in sequence with Arabic numerals. Each figure should be identified with a figure number on the back. Any lines, numbers, or lettering that are to appear in the illustrations should be large enough for the necessary reduction. Line drawings should be drawn with black India ink on white paper and should be about twice the size of the finished blocks. Graphs can be plotted on plain white or blue squared paper; grid lines that are to show in the engraving should be inked in black. In general, photographs should be about 1½ times the size of the final block and must be submitted as mounted glossy enlargements showing good detail and adequate, but not excessive, contrast. Authors should indicate in the manuscripts the approximate position of text figures.

Italics only are used for emphasis, especially for distinguishing titles of books and papers. It is marked in the manuscripts by underscoring.

References within the text should be indicated by numbers corresponding to those in the list of references. The list should be placed at the end of the paper and should contain no reading matter.

E.g.: 1. Barrow, William J.: *Restoration methods*. American Archivist 6 (1943): 151–54.

Authors alone are responsible for the opinions expressed in their papers.

50 offprints of each article will be sent to the author free of charge. Extra copies, if desired, will be supplied at a special rate.

© 1980 Munksgaard International Publishers Ltd. The appearance of the fee codes in this journal indicates the copyright owner's consent that copies or articles may be made for personal or internal use, or for the use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc., 21 Congress Street, Salem, Massachusetts 01970 for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. All other rights, including microfilm, reserved.

Editor's Address

Manuscripts and review copies of books should be sent to the editor: Poul A. Christiansen, Librarian. University Library: Scientific and Medical Dept., 49 Nørre Allé. DK-2200 Copenhagen N, Denmark.

Board of Editors

EDITOR:

POUL A. CHRISTIANSEN, Librarian. University Library: Scientific and
Medical Dept. DK-2200 Copenhagen N, Denmark.

ASSOCIATE EDITORS:

N. S. BAER, Professor. New York University, Institute of Fine Arts: Conservation Center. 1 East 78th
Street, New York, NY 10021, U.S.A.

GÜNTER BRANNAHL, Conservator. University Library. Prinzenstr. 1, D-3400 Göttingen, FR
Germany.

RICHARD D. SMITH, President. Wei T'o Associates, Inc. 224 Early Street, Park Forest, IL
60466, U.S.A.

CONSULTANT EDITORS:

ARIE ARAD, B.Sc., Chief of Restoration Section. Israel State Archives. Jerusalem, Israel.

TOM COLLINGS, Senior Lecturer. Camberwell School of Art and Crafts. Peckham Road, Lon-
don SE5 8 UF, England.

IAN COOK, Principal Conservator. National Library of Australia, Canberra ACT 2600, Au-
stralia.

FRANÇOISE FLIEDER, Directeur du Centre de Recherches sur la Conservation des Documents
Graphiques. 36 rue Geoffroy-Saint-Hilaire, F-75005 Paris, France.

TOMOKICHI IWASAKI, Director. 1-13-4 Ueno Sakuraghi, Taito-ku, Tokyo, Japan.

Y. P. KATHPALIA, M.Sc., Scientific Officer. National Archives of India. New Delhi 5, India.

ROMUALD KOWALIK, Professor, Head of Microbiological Laboratory. Institute of Industrial
Organic Chemistry. PL-03-236 Warsaw, Poland.

HELGA LAURENSZKY, Chem.Eng., Chief of Restoration Department, Hungarian National
Archives. Uri u. 54-56, H-1014 Budapest, Hungary.

FRANTIŠEK MARTINEK, Chief of the Department for Conservation and Restoration of Archival
Material. Státní ústřední archiv v Praze. Karmelitská 2, 11801 Praha 1 - Malá Strana, Czecho-
slovakia.

I. P. MOKRETSOVA, Dr., VNIIR. 10, Krestyanskaya pl. SU-109172 Moscow, U.S.S.R.

ROBERT C. MORRISON, Lecturer. Canberra College of Advanced Education, School of
Applied Science, Materials Conservation, P.O. Box 1, Belconnen ACT 2616, Australia.

YULIA PETROVNA NYUKSHA, Dr. (biol.sc.), Chief of the Department of Hygiene and
Restoration of Books. M. E. Saltykova-Shchedrin State Public Library of Leningrad, SU-191069
Leningrad, U.S.S.R.

ENRICA ORMANNI, Direttore. Centro di fotoproduzione, legatoria e restauro degli Archivi de
Stato. Via Constanza Baudana 14, I-00153 Rome, Italy.

JAN PIDEK, Head of Records Conservation Section. Public Archives. 395 Wellington Street,
Ottawa K1A 0N3, Canada.

GALINA S. ROZKOVA, Dr. (biol.sc.), Chief of the Department of Hygiene and Restoration of
Books. State V. I. Lenin Library of the U.S.S.R., SU-101000 Moscow, U.S.S.R.

ANDRÉE SCUFFLAIRE, Dr.Phil. L., Conservateur. Archives Générales du Royaume, B-1000
Bruxelles, Belgium.

NORMAN J. SHAFFER, Chief of Photoduplication Service. Library of Congress. Washington.
DC 20540, U.S.A.

CHANDRU J. SHAHANI, Ph.D., Chief of Document Preservation Branch. National Archives
and Records Service. Washington. DC 20408. U.S.A.

- 221 GRAVELL, T. L.: The Need for Detailed Watermark Research.
- 227 GUIDA, G., M. MARABELLI & I. REINDELL: Restoration and Storage of
Lead Artifacts.
- 81 KLIMENKO, G. K.: see A. M. POLISHKO.
- 99 KOWALIK, R.: Microbiodegradation of Library Materials Part 1, chap-
ters 1-3.
- 135 KOWALIK, R.: Microbiodegradation of Library Materials Part 2, chap-
ter 4. Microbiodecomposition of Basic Organic Library Materials.
- 115 KRINSKY, C. H.: see C. G. RAMBUSCH.
- 227 MARABELLI, M.: see G. GUIDA.
- 91 NAZAROVA, O. N.: see L. I. VORONINA.
- 71 NYUKSHA, J.: Biodeterioration and Biostability of Library Materials.
- 1 PARKS, E. J.: see W. K. WILSON.
- 91 PETUSHKOVA, Yu. P.: see L. I. VORONINA.
- 81 POLISHKO, A. M. & G. K. KLIMENKO: Storability of Film Sound Records.
- 115 RAMBUSCH, C. G. & C. H. KRINSKY: American Architectural Records:
Creating Order and Organization.
- 227 REINDELL, I.: see G. GUIDA.
- 123 ROZHKOVA, G. S.: On Preservation of Library Holdings.
- 91 VORONINA, L. I., O. N. NAZAROVA & Yu. P. PETUSHKOVA: Disinfection
and Straightening of Parchment Damaged by Microorganisms.
- 1 WILSON, W. K. & E. J. PARKS: Comparison of Accelerated Aging of Book
Papers in 1937 with 36 Years Natural Aging.
- 57 YUSUPOVA, M. V.: Conservation and Restoration of Manuscripts and
Bindings on Parchment.

ANNOUNCEMENTS and REPORTS of MEETINGS

- 239 THE COMMITTEE ON PRODUCTION GUIDELINES for BOOK LONGEVITY: Inter-
im Report on Book Paper, April 1981.
- 78 Fellowship Offered by the Smithsonian Institution.
- 79 Special Conference on Fumigants Plans Broad Strategy Covering Staff
Safety and Collections Care. Report Will Recommend Specific Steps
Applicable to All Museums Regarding Fumigation Procedure, Govern-
ment Responsibility, Research and Training.



RESTAURATOR

Contents 4: 3-4

- 135: R.KOWALIK: Microbiodeterioration of Library Materials Part 2, chapter 4. Microbiodecomposition of Basic Organic Library Materials.
- 221: T. L. GRAVELL: The Need for Detailed Watermark Research.
- 227: G. GUIDA, M. MARABELLI & I. REINDELL: Restoration and Storage of Lead Artifacts.
- 239: THE COMMITTEE ON PRODUCTION GUIDELINES FOR BOOK LONGEVITY: Interim Report on Book Paper, April 1981.

Indexed in:

Chemical Abstracts

Current Contents

Information Science Abstracts

Library Literature

Library Science

Social and Educational Science Citation Index