

## **MASS CONSERVATION OF ARCHIVAL AND LIBRARY MATERIALS**

**Arif KARADEMİR**

KSÜ Orman Fakültesi, Orman Endüstri Mühendisliği Bölümü, Kahramanmaraş

### **ABSTRACT**

Librarians and archivists are concerned about pages that become brittle and disintegrated as a consequence of ageing (1). This is a national problem in many countries as their valuable recorded collections, scientific chronicles and paper artefacts are being at a high risk of extinction (2, 3, 4). In this study after the paper deterioration is briefly summarised, the methods developed to save such documents and increase their serving time are reviewed.

### ***ARŞİV VE KÜTÜPHANE DÖKÜMANLARININ TOPLU OLARAK KORUNMASI***

### **ÖZET**

Yaşlanma sonucu meydana gelen kağıtların çürümeleri arşiv ve kütüphanelerde büyük problemler oluşturmaktadır. Değerli tarihi, bilimsel ve sanatsal milli değerlerin yok olma ile karşı karşıya kalması nedeniyle bu problem birçok ülkede ulusal bir meseledir. Bu çalışmada kağıtların yaşlanması kısaca özetlendikten sonra, bu dökümanların hizmet sürelerini uzatmak ve korumak için geliştirilmiş metodlara değinilmiştir.

### **INTRODUCTION**

The survey carried out in 1988 (5) revealed that in the United State 12 % of the modern collections of the National Library of Medicine are so embrittled that they can not be circulated to the users without a risk of irreparable damage. This was an equivalent of 158.000 volumes and each year an estimated 5.000 additional volumes become embrittled. The Library of Congress had also same problem as it's 25 % of 14 million books were then too brittle to circulate. Furthermore 77.000 books were reported to be added to this category every year. The problem of paper deterioration had devastating effects in all libraries in the United States. Therefore the issue was discussed in the Senate in October 11 1988. Then, the congress in the Joint Resolution 394 appropriated over \$ 100 million in support of the projects targeted to save their national recorded heritage.

The New York Public Library (NYPL) is now recognised nationally and internationally as a pioneer and leader in preservation planning (6). NYPL shares its expertise with others and runs training programs in paper conservation. Therefore many professionals from other countries frequently visit the centre and transform the

information in order to save their national library books. Between 1985 and 1987, countries interested in the centre include England, Scotland, Canada, Australia, Colombia, Mexico, Venezuela, France, the German Democratic Republic, South Africa, the Russia (then the Soviet Union) and the People's Republic of China.

### THE NATURE OF PAPER

Paper is built up at least a million components per gram, mainly fibre and filler particles. Raw materials include fibres that give the paper its mechanical stability, fillers that give optical properties and printability, and a multitude of chemical additives. The fibre material is generally wood-pulp fibre of mechanical or chemical origin. The paper made from mechanical pulp due to higher lignin content is likely to suffer more from ageing. The fillers are of inorganic origin, and include kaolin clay, calcium carbonate in the form of chalk or ground limestone, and speciality pigments like titanium dioxide that provide paper of high whiteness and high opacity. The chemical additives include hydrophobic agents that provide water and ink resistance, starch or other water-soluble polymers that provide dry or wet strength (7).

The cellulose, like most carbohydrates, can undergo an enormous variety of chemical transformations. The cellulose inside the microfibrils (ordered cellulose), however, is not easily degraded as the cellulose at the surfaces of the microfibrils and in structurally weakened zones (unordered cellulose). Three reactive hydroxyl groups two secondary (on carbon atoms in position 2 and 3) and one primary (on carbon atom number 6) attached to each beta-D-glucopyranose unit within the cellulose chain are very important in respect to cellulose degradation (8, 9) (Figure 1).

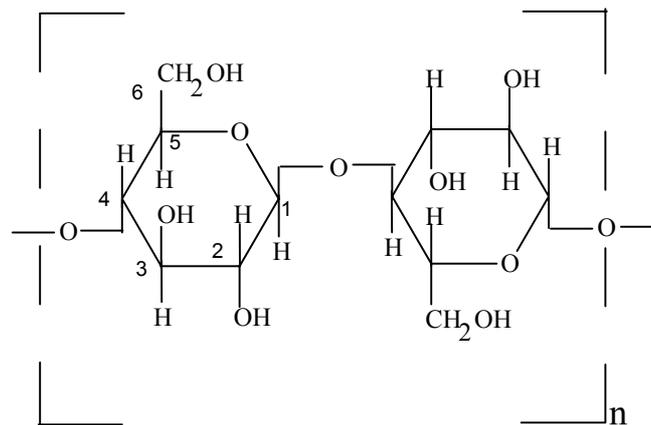


Figure 1: The Molecular Structure of Cellulose.

Lignin may degrade more rapidly than cellulose under the influence of oxygen and air, which results in the yellowing of paper. Hemicelluloses are hydrolysed more easily than both cellulose and lignin (10).

#### **Factor Effecting the Paper Deterioration**

The major cause of paper deterioration in libraries is the acid-catalysed hydrolysis of the cellulose fibres in paper. The most important source of acidity in book papers is the hydrolysis of the aluminium ion introduced during sizing as aluminium sulphate (papermaker's alum) ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ). The acids break down the cellulose, hemicellulose, and lignin in paper and form additional acids as by-products. As a result of this, paper strength is dramatically reduced. 80-90 % of paper decay in libraries is caused by the acid-catalysed hydrolysis (11).

The absorbance of acid compounds from atmosphere like  $\text{SO}_2$  and  $\text{NO}_x$  (12, 13, 14, 15) and the presence of the transition metal ions such as iron and copper also increase the paper degradation (16, 17). Presence of oxidative gases like  $\text{O}_3$  increases the rate of oxidation ion (14, 18). Some printing inks are also reported to cause degradation. Studies show that UV radiation causes photo-oxidation in the paper structure (19, 20). Deteriorations due to biological activities like insects and molds (fungi) are also another problem to be solved in paper preservation (21). The moisture and the cyclic changes in library atmosphere are believed to accelerate the degradation mechanism.

#### **THE HISTORY OF PAPER PRESERVATION**

As discussed above, the increase in acidity in the cellulosic materials are the main source of deterioration in the libraries. Therefore majority of studies in paper preservation are focused on deacidification methods. When a library with deteriorating books is imagined, it is well appreciated that the method must have a capacity to treat a quite big number of books. It should be also fast and economical. Manual treatment of materials, however, requires a long time and reported to be quite expensive.

Faraday (22) Calvert (23) and Latheby (24) were the first researchers to identify acid attacks as destructive to books and discussed the effects of air pollution from, then, mainly coal gas lamps.

Deacidification was first practiced at the Albert and Victoria Museum in London (25). Barium hydroxide dissolved in methanol was used to deacidify the canvases of oil paintings, which were deteriorating from sulphur dioxide or trioxide attack. Barrow refined the work of Schierholdtz, who had invented the aqueous deacidification using calcium bicarbonate aqueous solution (26), and improved his two-stage immersion process (27). In the first stage, books were immersed in a saturated solution of calcium hydroxide for 20 minutes then in the second stage materials were transferred into a saturated solution of calcium bicarbonate.

In 1972, the non-aqueous deacidification process was first used by Wei T'o Associates. The method was based on the introduction of carbon dioxide to form a

magnesium alkoxide containing methoxy carbonate radical (28). The company also used chlorofluorocarbon until it was identified as a harmful gas to the ozone layer. After that it was replaced with hydro-chlorofluorocarbon.

Ammonia, the first gaseous deacidification agent, was used during 1950's (28). Amines are derivatives of ammonia ( $\text{NH}_3$ ) where one or more of the hydrogen is substituted. The nitrogen, instead of an alkali or alkaline earth metal, produces the alkalinity for deacidification.

The mass deacidification procedures developed to date include vapour-phase and liquid-phase processes. For liquid phase techniques, aqueous and non-aqueous systems are applied. Whilst in the aqueous method, the dipping are performed, in non-aqueous process air and airless spraying, brushing are performed. Some procedures may also strengthen the paper as well as deacidifying it.

In general, the most important criteria for a suitable treatment can be listed as (29);

- 1- Complete, permanent and uniform neutralization of acid compounds present in the paper,
- 2- Deposition of an alkaline reserve in the paper in a suitable concentration,
- 3- Removal of other detrimental impurities,
- 4- Permanence of printing and stamping inks.

The commercially available mass deacidification methods are summarized below (30);

#### **1- DiEthylZinc (DEZ) Process**

Inventors: J. C. Williams and G. B. Kelly, Jr. (1974).

Deacidification agents: DiEthylZinc (DEZ).

Description: A gaseous phase mass deacidification system claimed to treat a minimum of 1.000.000 books annually. 5.000 to 10.000 books deacidified per 48- to 60-hour cycle.

#### **2- Wei T'o Non-aqueous Book Deacidification System**

Inventors: R. D. Smith (1965).

Deacidification agents: Methoxy magnesium methyl carbonate.

Description: Deacidification through wetting in a liquidified gas solution. Mass deacidification cycle requires 40 min and protects up to 60 books per cycle.

#### **3- Preservation Technologies Bookkeeper Process**

Inventors: R. A. Kundrot (1985).

Deacidification agents: Magnesium oxide powder.

Description: Books held open in special holder are immersed in a suspension of submicron magnesium oxide powder in trichlorotrifluoroethane. Treatment takes 3 hours and magnesium oxide particles are held in paper by electrostatic forces.

**4- Interleaf VPD Process**

Inventors: W. H. Langwell (1964).

Deacidification agents: Cyclohexylamine carbonate.

Description: Cyclohexylamine crystals in porous packets are placed in boxes containing documents. The crystals volatilize producing cyclohexylamine vapour, which deacidifies the paper. The process takes several days.

**5- Book Preservation Associates Ethanolamine Process**

Inventors: Unknown.

Deacidification agents: Mixture of monoethanolamine (ethanolamine), diethanolamine and triethanolamine.

Description: Books are treated inside a sealed shipping container. Mixture with moisture is introduced into the containers under a specific pressure and deacidify the materials. Residual ammonia and ethylene oxide are removed by vacuum.

Some of the mass conservations methods developed over the last 20 years are listed above. DEZ methods are one of the most used and accepted one as it has the highest capacity to treat the mass number of documents. It is reported that while the DEZ treatment of 1 m paper costs approximately 700 frank, it can be up to 3000 frank when manual treatment is chosen (31). Therefore the DEZ methods in details are discussed below.

**MASS DEACIDIFICATION WITH DEZ (DiEthylZinc) METHOD**

The treatment was successfully used by U.S. Congress in 1988 (32). The Dutch State Archives also applied the method in 1991 in order to deacidify their historical documents (Colonial Mail Report), which was equivalent to 1 billion books (33).

The DEZ process is based on gas diffusion. DEZ molecules penetrate between the leaves in an archives case or between the pages of closed books. The process is carried out in a specially designed deacidification chamber. The chamber diameter could be around 2 m and its length would be around 3 to 6 m. The whole DEZ treatment consists of three stages, which are drying, diffusion and dehydration (31).

**Drying**

Warm dry nitrogen is flushed through the deacidification chamber and this dries the paper and consequently leads to an increase in the amount of water in the vapour phase. Using vacuum, the water in the vapour phase is removed. The final water content of the paper after the drying stage is lower than 0.5 % by weight. During drying in general, four heating and cooling stages are performed from 35<sup>o</sup> C to a maximum of 54<sup>o</sup> C. The pressure is also changed from 1000 to 0.65 torr. After the drying phase, liquid nitrogen is flushed through the system in order to make the environmental inert.

### Diffusion

During the diffusion step, DEZ is introduced into the deacidification chamber to deacidify the papers using nitrogen gas as a carrier. The pressure is kept approximately at 15 torr while the temperature increases from approximately 21<sup>0</sup> C to 54<sup>0</sup> C. After this, excess of DEZ is removed by purging with nitrogen while the temperature is decreased to approximately 15<sup>0</sup> C.

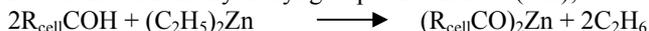
### Rehydration

Rehydration is the final stage in the whole process. Moisture is injected into the deacidification chamber at approximately 54<sup>0</sup> C to increase the moisture content of the deacidified materials before deacidification chamber is opened. After this stage, a 3-day humidification at 50 % RH (relative humidity) is carried out.

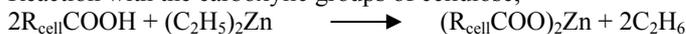
### Reaction Mechanisms in DEZ Method

DEZ reacts very rapidly with the organic as well as the inorganic compounds present in paper. The main reactions which will take place during the deacidification are (34, 35, 36);

Reactions with the hydroxyl groups of cellulose (cell);



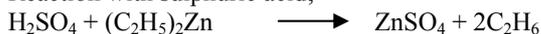
Reaction with the carboxylic groups of cellulose;



Mixed reactions with the hydroxyl groups and carboxylic groups of cellulose;

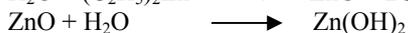
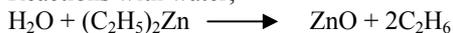


Reaction with sulphuric acid;



The zinc sulphate formed remains in the paper, while the ethane gas is removed.

Reactions with water;



Due to the lower moisture content of paper (0.5 %), most of the excess DEZ initially forms ZnO, which remains in the paper as an alkali-reserve. ZnO is amphoteric, dissolving in acids to form salts and in alkali to form zincates, such as  $[\text{Zn}(\text{OH})_3]^-$  and  $[\text{Zn}(\text{OH})_4]^{2-}$ . When ZnO dissolved in the water present in the paper, the pH of the treated paper could be around 7.5. ZnO can also react with alkaline compounds. Therefore the pH of the extract of the treated paper can never exceed the value of 9.5 according to the following reactions;



The remaining ZnO protects the paper against the acid-catalysed hydrolysis of the cellulose.

### **SOME ADVISES TO BOOKKEEPERS**

It is a well-known fact of the life that nothing can resist to ageing. Therefore things can be done only to increase the serving time of paper by eliminating and/or slowing down the reactions taking place in degradation mechanism.

Although Priest *et al* (37) stated from their extensive study that the lignin containing paper actually does not loose strength at a greater rate than comparable grades of paper containing little or no lignin during ageing, pulps containing lignin is normally not recommended for the use of archival and record documents. The colouring substances are believed to be mainly generated by lignin and lignin derivatives and generally attributed to structures such as quinines, quinine methides and stilbenes (38). Until the paper is formed in the paper machine, all potential metal ions and chemicals causing acidity later in sheet should be removed. In the same manner, aluminium should be avoided as well as rosin sizing. Paper must be produced in alkali/neutral system, which employs the calcium carbonate as filler. Calcium carbonate as a buffering chemical in paper balances the acidity and keeps the sheet neutral, which significantly increases the paper permanence. The printing materials should not cause or promote any degradation reactions. Environmental conditions, where printed records and documents are stored like library, must be specifically controlled under close monitoring. It is important to keep the temperature and humidity at predetermined level as well as not to allow any big cyclic change in climate. Precaution should be taken to avoid UV radiation. It is also important to provide a pollutant free environment. Some chemicals should be also used to control biological activities such as insects and microorganisms.

### **CONCLUSION**

As a result of ageing, the life span of extremely high volume of printed documents, which are used for record and storage purposes all over the world is dramatically reduced. This leads to an extensive, time consuming and highly costly restoration and replacement work. Some of the methods are summarised and DEZ method specially is explained due to its worldwide acceptance and uses.

Over the last two decades one of the remarkable change in the paper industry for the paper preservation is that the most of the paper mills in the world are now working in alkali/neutral system and making alkali papers. This is a result of partly public consciences, partly state legislation and partly market changes in the raw material reserves. However this does not mean that in the next century, the world civilisation would not face to the problem of paper deterioration. Overall, studies to understand the ageing mechanisms and to increase the serving time of the records and documents are to some extent to help reduce the deforestation in present time, where the high demand for paper is increasing and the raw materials are running out.

**REFERENCES**

1. GURNAGUL, N., HOWARD, R.C., ZOU, X., UESAKA, T., PAGE, D.H. 1993. The Mechanical Permanence of Paper: A Literature Review, *Journal of Pulp and Paper Science*, 19(4):160-166.
2. PELL, C. 1988. Senate Resolution 394 in Luner, P. (Ed.) *Paper Preservation Part I: Congressional Voices*, Syracuse, New York, p:10.
3. POOLE, F. 1972. Some Thoughts on Conservation of Library Materials, in Cunha, G. M. (Ed.) *Proceedings of the 1971 Seminar on the Application of Chemical and Physical Methods to the Conservation of Library and Archival Materials*, Library of Boston Athenaeum, Boston, p:13.
4. KELLY, G.B., Jr. 1980. *Non-Aqueous Deacidification: Treatment En Masse for the Small Workshop*. The International Conference on the Conservation of Library and Archive Materials and the Graphic Arts. Cambridge, England.
5. PELL, C. 1989. Senate Resolution 394 in Luner, P. (Ed.) *Paper Preservation Part I: Congressional Voices*, Syracuse, New York, p.10.
6. DEGENNARO, R. 1989. *Research Libraries: Mankind's Memory at Risk in Paper Preservation* (Ed) Luner, P. Tappi Press, p.19.
7. HAVERMANS, J. B.G.A. 1995. *Environmental Influences on the Deterioration of Paper*, Rotterdam, The Netherlands, p.17.
8. FLYNN, J. G., WILSON, W. K. 1958. Degradation of Cellulose in a Vacuum with Ultraviolet Light, *Journal of Research of The National Bureau of Standard*, 60, p.229.
9. FENGEL, D., WEGENER, G. 1989. *Wood: Chemistry, Ultrastructure and Reactions*, Walter De Gruyter, Berlin.
10. LANTING, R. W., LOGTENBERG, E. H. P., MUETGEERT, J., NIBOER, H., WESTRA, H. A. 1985. *Veroudering en Aantasting van Cellulose Door Luchtverontreiniging*, R 88/195, TNO, Delft, The Netherlands.
11. SMITH, R. D. 1983. *The History and Use of Magnesium Alkoxides in the Nonaqueous Deacidification of Books, Documents and Works of Art on Paper*. The 1983 Annual Meeting of International Arbeitsgemeinschaft Der Archiv-, Bibliothek-Und Graphikrestauratoren (IADA), The Hague, Netherlands.
12. ZOU, H., GURNAGUL, N., UESAKA, T. 1993. The Role of Lignin in Mechanical Permanence of Paper, Part I: Effect of Lignin Content, *J. Pulp and Paper Sci.*, 19(6):235.
13. RODENBURG, L. J. M. 1988. *ACBAM Phase 4: Measurements of the Deposition-Rates of Some Cellulose Containing Materials*, R 88/179A, TNO, Delft, The Netherlands.
14. DANIEL, F., FLIEDER, F., LECLERC, F. 1990. The Effects of Pollution on Deacidified Paper, *Restaurer*, No:11, p.179.
15. WILLIAMS II, E. L., GROSJEAN, D. 1990. *Exposure of Deacidified Paper to Ambient Levels of SO<sub>2</sub> and NO<sub>2</sub>*, Getty Conservation Institute, California.

16. TIMELL, T. E. 1965. Wood Hemicelluloses, Part II, *Advances in Carbohydrate Chemistry and Biochemistry*, No:20, p:409.
17. YOUNG, R. A., ROWELL, R. M. 1986. (ad.) *Cellulose; Structure, Modification and Hydrolysis*, New York, Wiley.
18. RODENBURG, L. J. M. 1988. *ACBAM Phase 4: Measurements of the Deposition-Rates of Some Cellulose Containing Materials*, R 88/179A, TNO, Delft, The Netherlands.
19. DANEAULT, C., ROBERTS, S., LEVESQUE, M. 1991. The Prevention of Light-Induced Yellowing of Paper: the Inhibition of Reversion By Merchants of TMP and CTMP From Balsam Fir (*Abies Balsamae*) and Black Spruce (*Picea Mariana*), *J. Pulp and Paper Sci.*, 17(6):187.
20. LEBE, S. E., LONSKY, W. F. W., MCDONOUGH, T. J., MEDVECZ, P. J. 1988. *International Pulp Bleaching Conference*, p:247.
21. RAYNES, P. 1986. *Insects and Their Control in the Library. Conservation Administration News*, No: 27/4.
22. FARADAY, M. 1843. *On Light and Ventilation. The Repertory of Patent Inventions and Other Discoveries and Improvements* 2:174-81 and 2:238-50.
23. CALVERT, F.C. 1851. *On Decay in the Binding of Books. Transactions of the Society of Arts* 57: 120-122.
24. LETHERBY, H. 1858. *Home Correspondence. Journal of the Society of Arts* 7:215-219.
25. BAYNES-COPE, A.D. 1969. *The Nonaqueous Deacidification of Documents*, *Restaurator*, 1(1):2-9.
26. SCHIERHOLTZ, O.J. 1936. U.S. Patent 2.033.452.
27. BARROW, W.J. 1976. *Deacidification and Lamination of Deeteriorated Documents. American Archivist*, 39:157-160.
28. SMITH, R.D. 1970. *Nonaqueous Deacidification of Paper and Books*, Ph.D. Dissertation, University of Chicago, Chicago.
29. BANIK, G. and SOBOTKA, W.K. 1989. *Deacidification and Strengthening of Bound Newspaper Through Aqueous Immersion in Paper Preservation* (ed) Luner, P. Tappi Press, p:138.
30. SMITH, R.D. 1989. *Deacidification Technologies: State of Art in Paper Preservation* (ed) Luner, P. Tappi Press, p:103.
31. MILLER, R. 1993. *The Deterioration of Modern Records and Books, and the DEZ Vapour Phase Process*. AKZO, Deer Park, Houston.
32. SEBERA, D.K., SPARK, P.G. 1989. *The Library of Congress DEZ Gas Diffusion Deacidification Process in Paper Preservation* (ed) Luner, P. Tappi Press, p:116.
33. HAVERMANS, J.B.G.A., VAN DEVENTER, R.J.P., STEEMERS, T.A.G. 1993. *Mass Deacidification of Archival Materials Using DEZ in Environmental Influences on the Deterioration of Paper* (ed) Havermans, B.G.A. 1995, University of Delft Press, p:149.

34. SAVVIN, N.N., GUTMAN, E.E., MYASNIKOW, I.A. 1981. Nature of Absorption Ventres of Atoms and Molecules of Oxygen on Metallic Oxides in Relation to Electrical Conductivity and Infrared Spectroscopic Data, *Russian Journal of Physical Chemistry*, 55:498.
35. SENGUPTA, G., AHLUWALIA, H.S., SEN, S.P. 1975. Zinc Oxide-Water Vapour System. Mechanism of Adsorption from Electrical Conductivity Studies, *Journal of Catalyses*, 36:111.
36. SENGUPTA, G., AHLUWALIA, H.S., SEN, S.P. and BANERJEE, B. 1979. Chemisorption of Water Vapour on Zinc Oxide, *Journal of Colloids and International Science*, 69:217.
37. PRIEST, D. J., STANLEY, J., KARADEMIR, A. 1997. Characteristics of Twentieth-Century Lignin-Containing Publication Paper, *Proceedings of the Fourth International Conference of the Institute of Paper Conservation*, London, UK, p:291.
38. WONG, P. T. T., HEREMANS, K. 1988. Pressure effects on protein secondary structure and hydrogen deuterium exchange in chymotrypsinogen, *Biochimica et Miophysica Acta*, 1, p:956.