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Mechanism of Autoxidative Degradation of Cellulose

by JANA KOLAR

INTRODUCTION

It is well documented that acid hydrolysis of cellulose and related carbohydrates is one of the key factors responsible for degradation of paper during ageing. A number of deacidification techniques have been developed to reduce the acidity and thus lower the deterioration of paper. However, while most treated papers degrade less rapidly, some results of accelerated ageing experiments show an increased degradation of papers whose pH has been changed from the acidic to the alkaline region using deacidification treatments. This phenomenon suggests the importance of degradative mechanisms other than acid hydrolysis.

The intention of this work is to survey the basic principles and the recent developments relating to the title area. Attention is drawn to the key factors which promote deterioration of cellulose under alkaline conditions and which form the basis for further stabilization studies.

The mechanism of light induced degradation of cellulosic and lignocellulosic material, of which several reviews have been published in the recent years is not included in this paper[1,2,3,4].

REACTIVE OXYGEN SPECIES

To understand the chemical reactivity of molecular oxygen, it is first necessary to discuss its electronic structure.

In O_2, the π^*_{2p} orbitals are half filled and there are three different states corresponding to different arrangements of these electrons. These states are, in order of increasing energy, $^3\Sigma^-_g$, $^1\Delta_g$, and $^1\Sigma^+_g$. The two unpaired electrons of a ground state molecular oxygen molecule have parallel spin (triplet spin state). In order to oxidize another atom or molecule by accepting a pair of electrons from it, both new electrons must be of parallel spin to fit into the vacant species in the π^* orbitals.

Most organic molecules are covalently bonded nonradicals and the two electrons forming a covalent bond have opposite spins in the same molecular orbital and the reaction is spin restricted.

The reactivity of molecular oxygen can be increased by exciting it to its singlet states thereby removing the spin restrictions. Once excited, O_2 can emit energy and relax back to the ground state or react directly with a substrate. The lifetime of $^1\Delta_g$ is relatively long due to the fact that its conversion to the ground state is spin forbidden and it is therefore possible to observe chemical reactions of this species.

In aqueous solutions, molecular oxygen is a fairly good oxidizing agent. During the reaction, oxygen may be reduced to water by one-electron transfer in four successive stages giving rise to intermediate products, namely, superoxide ($HOO^\bullet/O_2^{\bullet-}$), hydrogen peroxide ($H_2O_2$) and hydroxyl radicals ($HO^\bullet$). The reaction thermodynamics for these processes are strongly influenced by the solution matrix and its acidity. Mechanisms and standard potentials for reduction of active oxygen species in water (1 atm. O_2) at pH 7 are illustrated in Fig.1[5].

Due to the variety of redox potentials of active oxygen species, a large number of reactions with carbohydrates and lignins are possible. In addition, reactions between the products of the reduction of oxygen themselves occur.

Some reactions of the active oxygen species are listed in Fig. 2. One electron reduction of molecular oxygen results in the formation of the superoxide which is not able to abstract hydrogen atom from cellulose. It migrates through the material

$$\text{pH 7: } O_2 \xrightarrow{-0.16} O_2^{\bullet-} \xrightarrow{+0.89} \overbrace{HOOH \xrightarrow{+0.38} HO^- + HO^\bullet \xrightarrow{+2.31} 2HOH}^{+1.349}$$

Fig. 1: Standard potentials for reduction of oxygen species in water.

$R^\bullet + O_2^{\bullet-}$	$\longrightarrow$	ROO^-	1
$O_2^{\bullet-} + O_2^{\bullet-} + H_2O$	$\longrightarrow$	$O_2 + HOO^- + HO^-$	2
$HOOH + O_2^{\bullet-}$	$\longrightarrow$	$O_2 + HO^\bullet + HO^-$	3
$HOOH + M^{n+}$	$\longrightarrow$	$M^{(n+1)+} + HO^\bullet + HO^-$	4
$HOOH + M^{(n+1)+}$	$\longrightarrow$	$M^{n+} + HOO^\bullet + H^+$	5
$HOO^\bullet + M^{(n+1)+}$	$\longrightarrow$	$M^{n+} + O_2 + H^+$	6

Fig. 2: Some reactions of active oxygen species.

until it is eliminated by recombination (reaction 1) or disproportionation (reaction 2). In both reactions peroxides are formed, which can be reduced by the superoxide (reaction 3). Alternatively, some transition metals may catalyze homolytic decomposition of peroxides (reaction 4). In reactions 3 and 4, reactive hydroxyl radicals are formed. Due to their extreme reactivity[6] they react rapidly with a variety of organic and inorganic compounds.[7] Transition metal ions may be reduced to a lower oxidation state by peroxides (reaction 5) or superoxide (reaction 6).

AUTOXIDATIVE REACTIONS OF CELLULOSE

There is strong evidence to suggest that atmospheric oxidation plays an important role in ageing of paper. While not much research has been done on the mechanism of oxidative degradation of cellulose during ageing, the chemistry of oxidative reactions of carbohydrates in aqueous solutions or suspensions has been the subject of extensive studies, particularly in conjunction with biological processes, ageing of alkali cellulose and oxygen bleaching of cellulose.[8,9,10,11].

Since there seems to be a correlation between ageing of cellulose and these processes, we will first discuss how cellulose degrades under these conditions.

The fact that oxidation of cellulose by molecular oxygen in alkaline media is mainly a radical-chain mechanism was first proposed by Entwistle et al.[12,13] Like all chain reactions, the mechanism can be discussed in terms of initiation reactions during which free radicals are formed, propagation reactions during which free radicals are converted into other radicals, and termination reactions which involve the combination of two radicals with the formation of stable products.

INITIATION	$RH + O_2$	$\longrightarrow$	$R^\bullet + HOO^\bullet$	7
	$R^- + O_2$	$\longrightarrow$	$R^\bullet + O_2^{\bullet-}$	8
PROPAGATION	$R^\bullet + O_2$	$\longrightarrow$	$ROO^\bullet$	9
	$ROO^\bullet + R'H$	$\longrightarrow$	$ROOH + R'^\bullet$	10
	$ROO^\bullet$	$\longrightarrow$	$R^+ + O_2^{\bullet-}$	11
	$R^\bullet + R'H$	$\longrightarrow$	$RH + R'^\bullet$	12
	$RH + HO^\bullet$	$\longrightarrow$	$R^\bullet + HOH$	13
TERMINATION	$R^\bullet + HO^\bullet$	$\longrightarrow$	ROH	14
	$R^\bullet + O_2^{\bullet-}$	$\longrightarrow$	ROO^-	15
	$R^\bullet + R^\bullet$	$\longrightarrow$	$R\text{-}R$	16

Fig. 3: Radical-chain mechanism of the oxidation of cellulose.

Initiation of autoxidation

Autoxidation of cellulose starts by reaction of the substrate with molecular oxygen. In a pure cellulose molecule, only the terminal reducing groups are able to react spontaneously with the molecules of oxygen in their ground state (Fig. 3, reaction 7). Due to the low redox potential of O_2, reaction 7 is very slow, but is promoted by ionization of the substrate in alkaline media (reaction 8).

Since transition metal ions are almost inevitably present in cellulose fibres, the metal catalyzed decomposition of hydroperoxides and hydrogen peroxide (reaction 4 and 5), which are formed during the propagation reactions, is an additional source of free radical species.

Propagation

Molecular oxygen adds to the primary carbohydrate radicals at a virtually diffusion controlled rate to give a peroxyl radical (reaction 9), which can abstract a hydrogen atom from another carbohydrate molecule and thus propagate autoxidative reactions (reaction 10)[14]. However, most sugar peroxyl radicals rapidly eliminate $O_2^{\cdot -}$ (reaction 11)[15] so no such propagation of the radical chain reaction was observed during γ-radiolysis of glucose[16]. It seems that only the C(5)-peroxyl radical eliminates $O_2^{\cdot -}$ either slowly or not at all[17]. Some other substrate radicals which may form during the autoxidation process (acylalkyl, ß-hydroxyalkyl ...) are good hydrogen abstracting species and are able to propagate radical chain reactions (reaction 12). While superoxide is not able to abstract a hydrogen atom from D-glucose[16], hydroxyl radicals are unspecified in their reactions with carbohydrates and abstract hydrogen atoms bonded to carbon (reaction 13) in an almost statistical manner[18]. However, some results suggest that in reaction with hydroxyl radicals, the hydrogen atom from the C-1 carbon of cellulose, pectin and dextrane is not abstracted[19,20].The removal of oxygen bound hydrogen atom by hydroxyl radicals is much less likely.[18,21]

Termination

Chain termination is caused by the association of two radicals (for example, reactions 14–16).

The propagation reaction 11 seems to be of limited importance during autoxidation of cellulose, therefore the reaction chains might be relatively short. Instead, a nonchain radical mechanism may be the predominant reaction route during autoxidative degradation of cellulose.

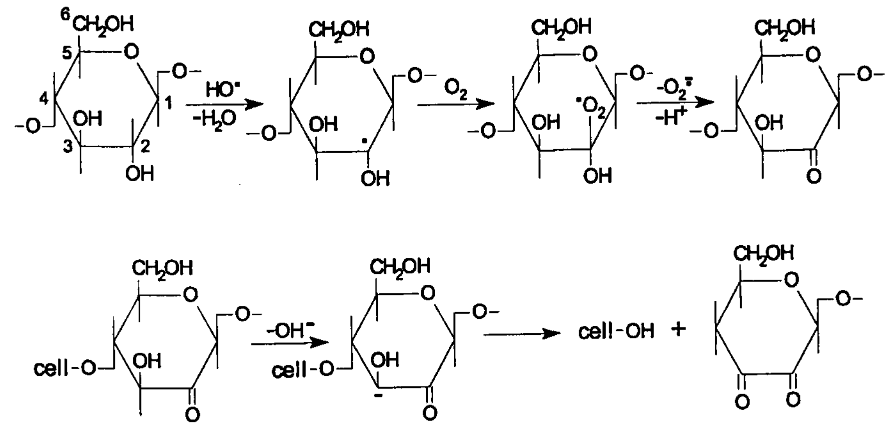

Fig. 4: Depolymerization of cellulose during autoxidative-alkaline degradation.

It seems that the main reaction leading to degradation of cellulose involves abstraction of carbon bound hydrogen atoms by hydroxyl radicals, resulting in the formation of hydroxyalkyl radicals. The latter are then converted into the corresponding carbonyl structures by oxygen. Carbonyl groups, which are formed on C-2, C-3 and C-6 atoms, then lead to the cleavage of glycosidic linkage according to the ß-alkoxy-elimination mechanism[22]. The reaction starting by abstraction of C-2 hydrogen atom is illustrated in Fig.4.

The glycosidic bond was found to be most labile in compounds containing carbonyl groups in position 2 or 3, while it is more stable in the case of C-6 aldehyde groups[23].

Some alternative routes which lead to the cleavage of the glycosidic linkage have been proposed, although the mechanistic details are not yet fully understood[24].

AUTOXIDATIVE DEGRADATION OF CELLULOSE DURING AGEING OF PAPER

Although research on the oxidative degradation of cellulose during ageing is scarce, some results strongly support the existence of the autoxidative mechanism described.

Thus it has long been known that the degradation of paper is significantly slower in the absence of oxygen[25]. Arney et al. demonstrated that strength loss of paper during ageing increased linearly with oxygen concentration, but did not go to zero in its absence[26]. Kleinert and Marraccini proved that peroxides are produced during ageing of paper[27]. Higher levels of peroxides were formed during ageing of bleached pulp at higher humidity than in a lower humidity environment and the total amount of peroxides increased linearly with time. Aldehyde groups formed by hydrolysis were found to be involved in peroxide formation[28]. Formation of peroxides during natural ageing was monitored using photographic materials[29]. Chemiluminiscence was used to follow radical formation at temperatures of 25 to 90°C[30]. During ESR studies, Wan et al. detected the presence of radical species in lignin containing paper, but not in papers made of pure cellulose[31]. It is possible that radical formation in the highly purified filter paper used in his study was below the threshold sensitivity of the method.

FACTORS PROMOTING AUTOXIDATIVE DEGRADATION OF PAPER

High pH

The rates of several of the reactions mentioned increase when the pH shifts from 7 to 10. However, the most important role of alkali is probably to promote the initiation reaction 1, which is catalyzed by ionization of substrate in alkaline media. In addition, the rate of the ß-alkoxy-elimination reaction of oxidized cellulose increases with increasing alkalinity of solution[32].

In our earlier work we have demonstrated that the presence of calcium carbonate stabilizes cellulose during ageing, while the addition of magnesium carbonate promotes degradation, as compared to the untreated pulp or that containing calcium carbonate[33]. This effect was ascribed to the rather high pH value of magnesium carbonate containing samples (ca. 10). However, sizing agents and additives can lower the pH of deacidified paper, and therefore paper containing magnesium carbonate does not necessarily degrade faster than that containing calcium carbonate[34].

Substances capable of autoxidation

Aldehyde groups

In a cellulose molecule, the only aldehyde group is the terminal one. However, in reality there are additional aldehyde groups which result from chemical processing of pulp and paper manufacturing. During ageing their content in cellulose increases due to the oxidative reactions. In addition, several low-molecular weight degradation products containing aldehyde moieties may be formed.

The presence of aldehyde groups may decrease the ageing resistance of alkaline paper in several ways. In addition to initiation of radical reactions (reaction 1), they

are also able to reduce Fe^{3+} to Fe^{2+} and thus compete with superoxide in reaction 6. The degradative effect of glucose during ageing of alkali cellulose[13] and oxygen-alkali bleaching of cellulose[35] has been well established.

It is important to note that while some of the aldehyde containing substances are removed during washing and aqueous deacidification, this does not happen during most non-aqueous treatments. As a consequence, aqueous deacidification may result in better stabilization of cellulose and paper.

Lignin

The role of lignin during ageing of paper is somewhat ambiguous.

It is known that lignin is capable of autoxidation and that the reaction is promoted by alkalinity of the solution[36]. It has been demonstrated that oxygen consumption of groundwood containing paper increases after the mass deacidification treatment[37]. Since lignin is able to react with oxygen, the oxidative degradation of the cellulose model substance methyl β-D-glucopyranoside is accelerated when various lignin model compounds are added to the solution[38,39,40]. Reactions of lignin model compounds with hydroxyl radicals and $O_2^{\cdot-}$ have been studied extensively by Gierer et al.[41,42]. Radicals react faster with lignin than with carbohydrate structures[43]; however, no stabilization of cellulose by the presence of lignin was observed during γ-irradiation experiments[20].

Despite these results, it has been shown that lignin exhibits an antioxidant effect in the presence of fat-soluble substances[44] and have been used to stabilize rubbers[45]. The stabilizing effect of lignin on the thermal stability of papers has lately been observed by several authors[46,47,48,49,50].

Effect of metal ions

The deleterious effects of iron and copper ions on the stability of cellulose and paper have been well documented[51,52].

Transition metal ions (M^{n+}, M^{n+1}) may participate in a number of important reactions, such as:

- Metal ion may be oxidized to a higher oxidation state by oxygen, which is reduced to superoxide.
- The free coordination site on some transition metal species can be considered as a large positive centre, capable of inducing a net dipole on the symmetric hydrogen peroxide molecule facilitating homolytic cleavage of H_2O_2 and the release of an hydroxyl radical. The transition metal in this case plays only a catalytic role, with no net change in its oxidation state.

- Formation of complexes with peroxides, which are further decomposed into free radicals and ions, according to reactions 4 and 5, where M^{n+} is a transition metal ion. Fe^{2+}, Cu^{1+} and some other transition metals ions react in this way. The most studied reaction is Fe^{2+} decomposition of hydrogen peroxide, also called the Fenton reaction (reaction 4)[53,54]. Reduction of ferric ions by many organic compounds as well as superoxide (reaction 6) allows these reactions to be repeated in a cyclic fashion, resulting in extensive oxyradical damage.

FACTORS INHIBITING AUTOXIDATIVE DEGRADATION OF CELLULOSE

The proposed mechanism suggests several possible ways of stabilizing cellulose and paper during ageing.

- The alkali chosen for deacidification should be such that the resulting pH of the paper after treatment is close to neutral, preferably below pH 9.
- The number of carbonyl groups can be effectively reduced by some reductive treatments. Reduction using sodium borohydride has been shown to increase the ageing stability of paper[55]. However, during the treatment, the aqueous solution of sodium borohydride decomposes. The resulting sodium borate may rise the alkalinity of paper and thus promote its degradation. It should therefore be removed from the paper after the treatment.
- Addition of antioxidants
  Inhibitors of oxidation processes are called antioxidants. According to their mechanism of action, they can be classified into two groups: preventive and chain-breaking antioxidants.

Preventive antioxidants

Antioxidants whose primary function is to interfere with the generation of free radicals are called preventive antioxidants. The most important preventive mechanism is usually peroxide decomposition in a process which does not involve the formation of free radicals. These antioxidants fall into two classes: stochiometric peroxide decomposers, such as phosphite esters which are reagents for the reduction of peroxides to alcohols, and catalytic peroxide decomposers. A variety of sulphur compounds fall into the latter class.

It has been demonstrated that iodide functions as a negative catalyst to protect cellulose from degradation during humid accelerated ageing.[51] It also protected paper containing zinc oxide during sun-lamp irradiation in a high humidity environment[56]. Although iodide and iodine have long been established as effective

$$2I^- + HOOH \longrightarrow I_2 + 2OH^- \qquad 17$$

$$2HO^- + I_2 + HOOH \longrightarrow 2I^- + 2H_2O + O_2 \qquad 18$$

Fig. 5 Catalytic heterogenous decomposition of peroxides

radical scavengers, Minor et al. suggested that the main stabilization of cellulose in borax solution at pH 9 occurs via catalytic heterogeneous decomposition of peroxides (Fig. 5, reaction 17 and 18)[57,58].

Besides peroxide decomposers, complexing agents, which have the ability to coordinate the vacant orbitals of transition metal ions to their maximum coordination number, are effective preventive antioxidants. The use of chelating agents such as EDTA is a popular method of controlling transition metal ions in many applications. However, copper[59] deactivation and iron[60] activation occurs with EDTA under oxygen pulping conditions. EDTA is not able to completely encompass the ferric ion[61] hence the complex is still able to react with peroxides[62]. The iron activation in the presence of EDTA was ascribed to an increase in the concentration of iron ions in solution.

EDTA appeared to have a negative effect on the ageing resistance of 17th century rag paper, while no effect on the stability of the paper, enriched with a mixture of ferrosulphate and tannin was observed[63].

On the other hand, it has been demonstrated that sodium phytate inhibits degradation of cellulose caused by iron-gall ink[64,65]. However, due to the high alkalinity of sodium phytate solutions, it promotes autoxidative degradation of paper. The latter problem can be avoided by the use of magnesium or calcium phytate[66].

Chain-breaking antioxidants

Chain-breaking antioxidants are able to react with radicals and convert them to more stable products.

A molecule will be able to act as a chain-breaking antioxidant under ambient conditions if it is able to donate a hydrogen atom rapidly to a radical and if the radical derived from the antioxidant is more stable than the starting radical, or is converted to other stable products.

Although addition of these antioxidants to inhibit degradation of paper during ageing has not yet been studied, the stabilizing effect of lignin on the stability of cellulose during thermal ageing is thought to be similar to that of hindered phenols, which are well known chain-breaking antioxidants. Thus it has been proposed that the consumption of peroxyalkyl and alkoxyl radicals by lignin blocks most of the cellulose degrading reaction pathways during ageing of paper[67]. In addition, phenoxy radicals which are formed during the reaction may scavenge some reactive radicals.

Conclusion

Despite our limited knowledge of the mechanisms leading to ageing of cellulose under neutral or alkaline conditions, some research results indicate the importance of autoxidative reactions. These seem to proceed by a variety of mechanisms, which generally involve substrate anion formation as the initial step and may continue via a free radical chain, or nonchain reaction pathways.

Understanding these mechanisms may help us in choosing the right treatment for certain paper, as well as form the basis for further stabilization studies. This work is in progress.

Summaries

Mechanism of autoxidative degradation of cellulose

The possible mechanisms of autoxidative degradation of cellulose are listed and their importance in degradation of paper during ageing is analysed. It is pointed out that autoxidative reactions are accelerated in alkaline media. In addition, certain transition metal ions as well as groups, which are capable of autoxidation, also promote the free radical reactions. Understanding of the main degradative routes may help us in choosing the right conservation treatment for certain paper, as well as form the basis for further stabilization studies.

Mécanisme de dégradation auto-oxydative de la cellulose

On a recensé les mécanismes possibles de dégradation auto-oxydative de la cellulose et on a analysé leur importance sur la dégradation du papier au cours de son vieillissement. On a observé que les réactions auto-oxydatives s'accélèrent en milieu alcalin. En plus certains ions de métaux transitoires ainsi que des groupements d'ions qui sont susceptibles d'auto-oxydation favorisent aussi les réactions de radicaux libres. La compréhension des principaux mécanismes de dégradation pourrait nous aider à choisir le traitement de conservation approprié pour certains papiers déterminés, et elle pourra aussi être le point de départ pour de plus amples études sur la conservation.

Vorgänge beim autoxidativen Abbau von Cellulose

Es werden die denkbaren Vorgänge des autoxidativen Abbaus von Cellulose aufgezählt und hinsichtlich ihrer Bedeutung für die Alterung von Papier bewertet. Es wird herausgestellt, daß diese

Vorgänge im alkalischen Bereich verstärkt ablaufen. Darüber hinaus werden Reaktionen an freien Radikalen auch durch bestimmte Übergangsmetalle befördert sowie durch Gruppierungen, die der Autoxidation zugänglich sind. Das richtige Verständnis für die wichtigsten Abbauvorgänge mag zur Wahl der richtigen Konservierungsmaßnahme für bestimmte Papiere beitragen, und ebenso ist es der Ausgangspunkt für weitere konservierungskundliche Untersuchungen.

References

1. Leary, G.J.: *Recent progress in understanding and inhibiting the light-induced yellowing of mechanical pulps.* J. Pulp Pap. Sci. 20 (1994): J154–160.
2. Heitner, C.: *Light-induced yellowing of wood-containing papers.* Heitner, C., Scaiano, J.C., eds.: Photochemistry of Lignocellulosic Materials. Advances in Chemistry Series, 531. Pointe Claire, Canada. American Chemical Society 1993: 192–204.
3. Hon, D.N.-S., & N. Shiraishi, eds.: *Wood and Cellulosic Chemistry.* New York: Marcel Dekker, Inc. 1991: 525–555.
4. Forsskahl, I.: *Towards an understanding of the photoyellowing of pulps and papers. Trends in Photochem.* Photobiol. 3 (1994): 503–519.
5. Sawyer, D.T.: *Oxygen Chemistry.* New York, Oxford: Oxford press 1991: 21.
6. Barnes, A.R., & J.K. Sugden: *The hydroxyl radical in aqueous media.* Phar. Acta Helv. 61 (1986): 218–227.
7. Buxton, G.V., & A.J. Elliot.: *Rate constants for reaction of hydroxyl radicals with bicarbonate ions.* Radiat. Phys. Chem. 27 (1986): 241–243.
8. Golova, O.P., & N.L. Nosova: *Degradation of cellulose by alkaline oxidation.* Russ. Chem. Reviews 42, (1973): 327–338.
9. von Sonntag, C.: *Free-radical reactions of carbohydrates as studied by radiation techniques.* Adv. Carbohyd. Chem. Biochem. 37 (1980): 7–77.
10. Gratzl, J.S., J. Nakano, & R.P. Singh, eds.: *The chemistry of delignification with oxygen, ozone and hydroperoxides.* Tokyo: Uni Publishers Co. Ltd. 1980.
11. Gratzl, J.S.: *Die chemischen Grundlagen der Zellstoffbleiche mit Sauerstoff, Wasserstoffperoxid und Ozon – ein kurzer Überblick.* Das Papier 10A (1992): V1–V8.
12. Entwistle, D., E.H. Cole & N.C. Wooding: *The autoxidation of alkali cellulose. Part I: An experimental study of the kinetics of the reaction.* Textile Res. J. 9 (1949): 527–546.
13. Entwistle, D., E.H. Cole & N.C. Wooding.: *The autoxidation of alkali cellulose. Part I: An experimental study of the kinetics of the reaction.* Textile Res. J. 10 (1949): 609–624.
14. Adams, G.E., & R.L. Willson: *Pulse radiolysis studies on the oxidation of organic radicals in aqueous solution.* Trans. Faraday Soc. 65 (1969): 2981–2987.
15. Bothe, E., D. Schulte-Frohlinde & C. von Sonntag: *Radiation chemistry of carbohydrates Part 16. Kinetics of HO2. Elimination from peroxyl radicals derived from glucose and polyhydric alcohols.* J. Chem. Soc. Perkin Trans. 2 (1978): 416–420.
16. Schuchmann, M.N., & C. von Sonntag: *Radiation chemistry of carbohydrates. Part 18. Free radical induced oxidation of neutral aqueous solutions of D-glucose in the presence of oxygen.* Z. Naturforsch. Teil B. 33 (1978): 329–331.
17. von Sonntag, C., & H.P. Schuchmann: *The elucidation of peroxyl radical reactions in aqueous solution with the help of radiation-chemical methods.* Angew. Chem. Int. Ed. Eng. 30 (1991): 1229–1253.

18. Schuchmann, M.N., & C. von Sonntag: *Radiation chemistry of carbohydrates. Part 14. Hydroxyl radical induced oxidation of D-Glucose in oxygenated aqueous solution.* J. Chem. Soc. Perkin. Trans. 2 (1977): 1958–1963.
19. Chirat, C., & D. Lachenal: *The effect of hydroxyl radicals on cellulose and pulp and their occurrence during ozone bleaching.* 8th Int. Symp. Wood Pulp. Chem, Helsinki, 1 (1995): 293–300.
20. Gilbert, B.C., M.D. King & C.B. Thomas: *The oxidation of some polysaccharides by the hydroxyl radical: an E. S. R. investigation.* Carbohydr. Res. 125 (1984): 217–235.
21. Asmus, K.-D., H. Möckel & A. Henglein: *Pulse radiolitic study of the site of OH. Radical attack on aliphatic alcohols in aqueous solution.* J. Phys. Chem. 77 (1973): 1218–1221.
22. Haskins, J.F., & H.J. Hogsed: *Alkali oxidation of cellulose. Degradative oxidation of cellulose by hydrogen peroxide in the presence of alkali.* J. Org. Chem. 15 (1950): 1264.
23. Theander, O.: *Polysaccharide modifications occuring in bleaching.* Tappi, 48 (1965): 105–110.
24. Schuchmann, M.N., & C. von Sonntag: *The effect of oxygen on the hydroxyl radical induced scission of glicosidic linkage of cellobiose.* Int. J. Radiat. Biol., 34 (1978): 397–400.
25. Major, W.D.: *The degradation of cellulose in oxygen and nitrogen at high temperatures.* Tappi 41 (1958): 530–544.
26. Arney, J.S., & A.J. Jacobs: *Accelerated aging of paper.* Tappi, 62 (1979): 89–91.
27. Marraccini, L.M., & T.N. Kleinert: *Aging and colour reversion of bleached pulps. Part I. Peroxide formation during aging.* Svensk Papperstidn. 65 (1962): 126–131.
28. Kleinert, T.N., & L.M. Marraccini: *Aging and colour reversion of bleached pulps. Part II. Influence of air and moisture.* Svensk. Papperstidn. 66 (1963): 189–195.
29. Daniels, V.: *Monitoring the autoxidation of paper using photographic materials.* Needles, H.L. & S.H. Zeronian, eds.: Conservation, Degradation and Characterization of Paper. Advances in Chemistry Series, 212, Philadelphia, USA. American Chemical Society 1986: 317–327.
30. Kelly, G.B., & J.C. Williams: *The use of chemiluminiscence in the study of paper permanene.* Eby, R.K. ed.: Durability of Macromolecul Materials. Advances in Chemistry Series, 95, Washington D.C: American Chemical Society 1979: 117–125.
31. Wan, J.K.S., M.Y. Tse & C. Heitner: *An ESR ant time-resolved CIDEP study of the light-induced yellowing processes of TMP paper.* J. Wood Chem.Technol. 13 (1993): 327–348.
32. Luetzow, A.E., & O. Theander: *0.6-aldehydocelluloses – thermal instability, β-elimination and acid hydrolysis.* Svensk Papperstid. (1974): 312–318.
33. Kolar, J., & G. Novak: *Effect of various deacidification techniques on the stability of cellulose pulps.* Restaurator 17 (1996): 25–31.
34. Kolar, J., & G. Novak: *Deacidification of paper – a progress report.* To be published in the Proceedings of International Book and Paper Conservation Conference, Ljubljana, Slovenia 1996.
35. Ericsson, B., O. Lindgren & O. Theander: *Factors influencing the carbohydrate degradation under oxygen-alkali bleaching.* Svensk Papperstid. (1971): 757–765
36. Gellerstedt, G., & B. Pettersson: *Autoxidation of lignin.* Svensk Papperstidn. (1980): 314–318
37. Dufour, J., & J.B.G.A. Havermans: *The accelerated deterioration of deacidified paper by autoxidation.* Proc. ARSAG Conference 1997, Posters: 334–335.
38. Theander, O., B.O. Lindgren & B. Ericsson: *Factors influencing the carbohydrate degradation under oxygen-alkali bleaching.* Svensk Papperstid. (1971): 757–765.
39. Yasumoto, M., Y. Matsumoto & A. Ishizu: *A model study on the degradation mechanism of carbohydrate during oxygen delignification.* roceedings of 7th International Symposium on Wood and Pulping Chemistry, 1, Beijing, China 1993: 192–196.

40. Yokoyama, T., Y. Matsumoto & G. Meshitsuka: *A model study on the degradation mechanism of carbohydrate during oxygen bleaching.* Proceedings of 8th International Symposium on Wood and Pulping Chemistry, 1, Helsinki, Finland 1995: 315–322.
41. Gierer, J., E. Yang & T. Reitberger: *On the significance of superoxide radical in oxidative delignification, studied with 4-t-Butylsyringol and 4-t-Butylguaiacol.* Holzforschung 46 (1992): 495.
42. Gierer, J.: *The chemistry of TCF bleaching.* Proceedings of 8TH International Symposium on Wood and Pulping Chemistry, 1, Helsinki, Finland 1995: 285–291.
43. Ek, M., J. Gierer, K. Jansbo & T. Reitberger: *Study on the selectivity of bleaching with oxygen-containing species.* Holzforschung 43 (1989): 391–396.
44. Catignani, G.L., & M.E. Carter: *Antioxidant properties of lignin.* J. Food Sci. 47 (1982): 1745
45. DePaoli, M.A., & L.T. Furlan: *Sugar cane bagasse-lignin as a photo stabilizer for butadiene rubbers.* Polym. Deg. Stab. 11 (1985): 327–337.
46. Abadie-Maumert, F.A., & N.A.Soteland: *Resistence des CTMP ou Viellissement.* Revue A.T.I.P. 44 (1990): 223–232.
47. Oye, R., T. Okayama, H. Matsubanra & K. Hanamura: *Studies on the degradation of paper and conservation. II. Degradation of mechanical-pulp containing paper.* J. Japan Tappi, 45 (1991): 61–68.
48. Lystad, E.: *Aging stability of high yield pulps.* Proceedings of the 18th International Mechanical Pulping Conference, Oslo, Norway 1993: 340–349.
49. Zou, X., N. Gurnagul & T. Uesaka: *The role of lignin on the mechanical permanence of paper. I. Effect of lignin content.* J. Pulp Paper Sci. 19 (1993): J235– 239.
50. Schmidt, J.A., C.S. Rye & N. Gurnagul: *Lignin inhibits autoxidative degradation of paper.* Polym. Deg. Stab. 49 (1995): 291–297.
51. Williams, J.C., C.S. Fowler, M.C. Lyon & T.L. Merril: *Metallic catalysts in the oxidative degradation of paper.* Williams, J.C. ed.: Preservation of Paper and Textiles of Historic and Artistic Value. Advances in Chemistry Series, 164. Washington D.C. American Chemical Society 1977: 37–61.
52. Shahani, C.J., & F.H. Hangemihle: *The influence of copper and iron on the permanence of paper.* Needles, H.L., Zeronian, S.H., eds.: Historic Textile and Paper Materials. Conservation and Characterization. Advances in Chemistry Series, 212. Phyladelphia, USA. American Chemical Society 1986: 387–410.
53. Walling, C.: *Fenton's reagent revisited.* Acc.Chem.Res. 8 (1975): 125–131.
54. Walling, C., in: King, T.E., H.S. Mason & M. Morrison, eds.: *The nature of primary oxydants in oxydations mediated by metal ions.* Proceedings of the 3rd International Symposium on Oxidases Related Redox Systems. Oxford. Pergamon 1982: 85–97.
55. Tang, L.C.: *Stabilization of paper through sodium borohydride treatment.* Needles, H.L., Zeronian, S.H., eds.: Historic Textile and Paper Materials. Conservation and Characterization. Advances in Chemistry Series, 212. Phyladelphia, USA. American Chemical Society 1986: 427–441.
56. Kelly, G.B., & J.C. Williams: *Inhibition of light sensitivity of papers treated with diethyl zinc.* Williams, J.C. ed.: Preservation of Paper and Textiles of Historic and Artistic Value II. Advances in Chemistry Series, 193. Washington D.C.: American Chemical Society 1981: 109–117.
57. Minor, J.L., & N. Sanyer: *Oxygen/alkali oxidation of cellulose nd model alcohols and the inhibition with iodide.* J.Polym.Sci. Part C 36 (1971): 73–84.
58. Minor, J.L., & N. Sanyer: *Carbohydrate stabilization with iodide in oxygen bleaching of kraft pulps.* Tappi 57 (1974): 109–112.
59. Abrahamsson, K., & O. Samuelson: *Oxygen-alkali cooking of wood meal. Part III. Influence of oxygen pressure, carbon dioxide and metal compounds.* Svensk Papperstid. 76 (1973): 480.

60. Samuelson, O., & L. Stolpe: *Degradation of carbohydrates during oxygen bleaching.* Svensk Papperstid. (1871): 545–552.
61. Lind, M.D., J.A. Hamor & J.L. Heard: *Stereochemistry of ethylenaminetetraacetat complexes.* Inorg. Chem. 3 (1964): 34–44.
62. Bull, C., G.J. McClune & J.A. Fee: *The mechanism of iron EDTA catalyzed superoxide dismutation.* J. Chem. Soc. 105 (1983): 5290–5300.
63. Porck, H.J., & W. Castelijns: *A study of the effects of iron and copper on the degradation of paper and evaluation of different conservation treatments.* Preprints of the International Congress of IADA, Uppsala, Sweden. 1991: 1–7.
64. Neevel, J.G.: *Phytate: a potential conservation agent for the treatment of ink corrosion caused by irongall inks.* Restaurator 16 (1995): 143–160.
65. Neevel, J.G.: *The development of a new conservation treatment for ink corrosion, based on the natural anti-oxidant phytate.* Preprints of the International Congress of IADA, Uppsala, Sweden. 1995: 93–99.
66. Neevel. J.G. Presentation at the European workshop on irongall-ink corrosion, Rotterdam: 1997.
67. Heitner. C.: *The chemistry and physics of lignin relating to mechanical permanence of lignin-containing papers.* Proceedings. Workshop on the Effects of Aging on Printing and Writing Papers, Philadelphia, USA. ASTM Institute for Standards Research 1994: 72–82.

Jana Kolar
National and University Library
Turjaška
SI-1000 Ljubljana
Slovenia

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Protection and Conservation of Materials on Paper

Evaluation of Permanence and Durability of the Laminated Material on Paper

by Meta Černič Letnar & Jedert Vodopivec

Paper as a carrier of cultural heritage

Conservation of books and documents in libraries and archives throughout the world, especially of those from the 19th and 20th century, showing signs of progressive decay, has become very urgent and demands immediate and effective measures – today approximately 70% of materials from the 19th century is beyond repair. Generally observed, a great number of more recent materials, which are about 50 to 150 years old, shows signs of very rapid decay, particularly in comparison to older materials dating back to the Middle Ages and up to the first half of the 19th century, which have remained in a perfectly good condition to the present day. The writing basis of older materials is hand-made paper from neutral raw materials of high quality and is still nowadays well preserved, whereas the materials – written, drawn or printed – on industrial acid paper in the last 150 years exhibit serious damage even when stored under appropriate conditions.

In recent years, the unregulated use of recycled kinds of paper in particular, being in striking contrast with regard to quality when compared to more durable kinds of paper, has become increasingly alarming and their use for materials of permanent value established as wholly inadequate.

With the aid of development and research in the field of the evaluation of quality of older kinds of materials as well as more recent kinds of paper, and using the conservation method of mass neutralisation and also some latest conservation-restoration techniques for the damaged materials, at present, many millions of books and a tremendous amount of archive materials are being saved. It has nowadays become the inevitable concern of every nation to preserve the national heritage and this is being solved in various ways, mostly within the available resources. A similar obligation for the future would be to ensure that the paper of the future will also be of use in the centuries and millennia to come, i.e. to ensure its utmost "longevity".

PRESERVATION OF THE WRITTEN CULTURAL HERITAGE
nowadays and for the future

OLDER KINDS OF DAMAGED WRITTEN MATERIALS ON PAPER
mass neutralization and latest conservation-restoration techniques

WRITTEN MATERIALS
nowadays and for the future
use durable kinds of permanent paper for written, printing and copy materials of permanent value

Fig. 1: Preservation of the written cultural heritage nowadays and for the future.

We have to be aware that through chemical procedures of the mass neutralisation of materials on acid paper the gradual process of deterioration is not halted, but only temporarily held back. Therefore, before any chemical procedure of neutralisation has been set in motion, it is necessary to observe some basic conditions for preventing and protecting the materials treated. At the same time the practical environment should be considered as much as possible.

Paper has always been and will also remain one of the most important transmitters and carriers of the written cultural heritage. However, paper is not eternal since it is made from relatively unstable organic raw materials and is thus more or less subject to ageing: its characteristics change and its quality is limited in the course of time. The mechanism of ageing is influenced by numerous interactions between substances in the paper and in its surroundings which are visible mostly in the deterioration of mechanical resistance, chemical stability and optical characteristics of paper.

The influence of internal factors on the ageing of paper represents an 80–85 % share – depending on paper producers and processors – mostly in the graphics branch, whereas the share of the external factors' influence is as low as 10–15 % and is in correlation to consumers in archives, libraries, museums, galleries and government institutions.

The protection of the written cultural heritage is a very complex and extensive subject on the influence of internal and external factors on ageing of materials on paper, demanding a high degree of co-operation from all the parties concerned including adequate governmental support.

STUDY OF PERMANENCE AND DURABILITY OF THE LAMINATED MATERIAL ON PAPER

In the framework of research on "Ageing of Paper and Cardboard" we have investigated the influence of the quality of paper and the conservation methods of lamination and coating on its permanence and durability, and on material on paper, under extreme conditions of accelerated ageing, with a raised temperature and relative atmospheric humidity, but without exposure to light.

Method of preservation of material on paper with lamination

Lamination is a method where a document on paper is reinforced on one or both sides with material that enhances its resistance, which is necessary for its better protection and conservation. The coating should be as thin and transparent as possible, except in cases where there is no writing on one side, where a document can then be strengthened with a more compact, non-transparent material.

Lamination is a method of conservation which cannot always be recommended due to its irreversibility and because it lessens the quality of a document to some extent: the document's originality is impaired. It is recommended for the protection of documents which have reached a stage of great fragility (weak mechanical resistance) so that no other method of preservation can be applied. It is also suitable for documents that have been burnt or the text comprised due to running inks and pigments on extremely damaged, decaying paper.

Before we started with the procedure, the quality of all materials to be used in the process of lamination had to be verified; the optimum conditions of pressure, temperature and time of application for lamination or coating were defined separately on every machine. Only in this way can we be spared the possible difficulties during the process of conservation or even the damage or complete destruction of the document in question.

The conservation method of lamination dealt with in this study was performed in the ARS workshop, on the machine for lamination and coating. ICP-PP-3 permanent paper, grammage 110 g/m^2, was used as a basis for a document of high quality. For the protective foil 1 the known polymer foil PE was applied, and for foil 2 a more recent polymer foil coated with thin Japanese paper and recommended by its producer for the protection and restoration of documents on paper. In our workshop two kinds of laminate composites were prepared.:

- Laminate composite LK-1: Japanese paper – PE foil – PP-3 permanent paper – PE foil – Japanese paper. Temperature: 100-110°C
- Laminate composite LK-2: Filmoplast R * – PP-3 permanent paper – Filmoplast R. Temperature of 110-125 °C

* Commercial product, available via relevant suppliers: thin paper coated with an acrylic. Producer: Neschen International.

The pressure was the same in both tests.

Methods of testing

A sample of paper and both samples of laminate composite LK-1 and LK-2 were exposed to conditions of accelerated ageing according to ISO 5630/3, at 80°±1°C and 65+/-2% relative atmosphere humidity, in a climatic chamber without exposure to light, over longer periods of time: 6, 12 and 24 days.

All climatized samples, paper as well as composites, were examined before and after accelerated ageing to determine their permanence and durability, following the standard methods for individual characteristics, such as:

- basic characteristics: grammage, voluminosity, contents of humidity, ash and filling
- chemical stability: pH, degree of polymerisation (viscosity-CED), degree of oxidation (Cu number);
- surface properties: porosity, wetting with water;
- mechanical resistance: tensile breaking strength, elongation, burst and tear resistance, folding endurance, stiffness;
- optical stability: whiteness, brightness, yellowness, opacity, diffusion and absorption of light.

Evaluation of quality of the laminated materials on paper – results and commentary

The attained values of measurement before and after accelerated ageing on the samples of paper and laminated composites with regard to the definition of their basic characteristics, chemical stability, mechanical resistance, surface properties and optical stability, have given the results which are shown in individual graphs.

BASIC CHARACTERISTICS

The tests on the influence of accelerated ageing on the samples of permanent paper and both samples of laminated composite have shown that there is no change in the obtained values in the grammage, voluminosity and content of humidity, ash and filling. Generally it can be said that some barely perceptible changes can be attributed to the unevenness and non-homogeneity of separate samples, which are a result of the technological conditions of production.

CHEMICAL STABILITY AND SURFACE PROPERTIES

With the aid of several conventional chemical methods individual reactions of decomposition of the cellulose molecule in a paper sample as well as decomposition of polymer foils in a composite were investigated.

Chemical stability of the chosen papers before and after ageing was tested according to the method of measuring pH of the extract and pH at the surface, viscosity-CED and Cu number.

Viscosity

The hydrolytic and oxidative decomposition of the cellulose molecule is assessed by a reduction of an average molar-mass or the degree of polymerisation, defined by determining a change and decrease of viscosity in the accelerated paper ageing process.

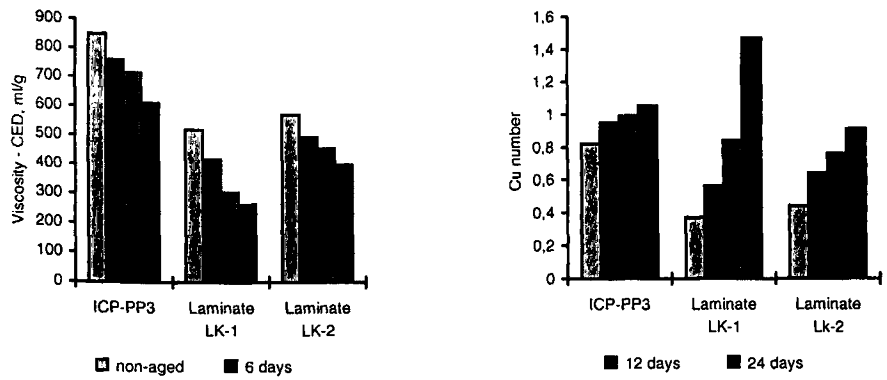

Fig. 2: Hydrolytic and oxidative decomposition of cellulose molecule chain and polymer materials: viscosity-CED and Cu number.

In Fig. 2 the depolymerization of a cellulose molecule in paper is shown by an assessment of viscosity according to the CED method. The greatest reduction of viscosity was observed in laminate composite LK-1, having the worst initial values and degradation through ageing being the greatest compared to the initial stage. The best results in this respect were achieved with the sample of paper itself.

Cu number

The conditions of ageing increase the number of reductive groups from the cellulose and hemicelluloses which, in the process of oxidation, turn from hydroxyl ones into aldehydes; the greater the degree of oxidation, the bigger the Cu number.

The measurement results of the Cu number are given in Fig. 2 and show an increase of oxidative decomposition in paper in both samples of the laminate composite. The oxidative decomposition is by far the greatest, especially with regard to the initial stage, in the laminate LK-1 sample. This was also confirmed by the measurement results of the surface IR spectrum: In ageing after 12 days visible oxidation products of decomposition are present; the laminate LK-2 sample shows favourable results of oxidative decomposition also in comparison to paper.

Porosity, pH surfaces, hydrophilicity , hydrophobicity

The influence of the conditions of ageing on possible changes of the surface porosity (the Gurley method), on changes of surface pH and on the angle of wetting with water (hydrophilicity and hydrophobicity of a surface as regards water) were examined.

On the basis of the measurement results it can be stated that ageing does not change the porosity to a great extent. Paper showed the same degree of permeability to air as before the ageing process; both laminate samples also remained perfectly non-porous and impermeable to air.

In Fig. 3 we can observe that the pH surfaces on all tested samples change and drop from the alkaline into the neutral range, which is especially visible on the samples of paper and laminate LK-2, whereas in the laminate LK-1 sample the pH value drops into the acid range, pointing to the presence of oxidative acid products, which are certainly undesirable with regard to future use.

The results of the contact angle of wetting measurements also show in Fig. 3 that with all the samples tested (paper as well as both composites) their resistance

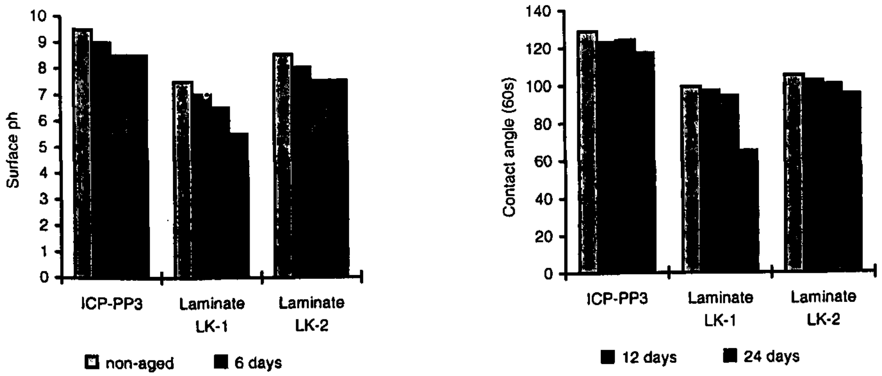

Fig. 3: Surface properties: Change of surface pH and surface hydrophilicity to water, measured with contact angle of wetting.

to water gradually decreases, that is to say, the surface becomes more hydrophilic to water – an undesirable effect from a consumer's point of view since it reduces the durability of a material to external influences.

Favourable results were obtained with the samples of paper and laminate LK-2, where the surfaces remained rather hydrophobic to water even over extended periods of time. A very bad result was obtained with the laminate LK-1 sample where already the initial values were lower compared to the other two samples and got worse over a period of time: the surface became completely hydrophilic.

MECHANICAL RESISTANCE

Mechanical resistance of paper with regard to ageing is influenced by reactions of fibres in the paper (the fibre-fibre link) and reactions within the cellular wall of fibres, and in the polymer materials by the quality of basic substances. An alteration (reduction of mechanical resistance) is brought about by chemical reactions of hydrolytical and oxidative disintegration resulting in the weakening of bonds between the fibres. Due to the process of entanglement, and the inner and outer connections between the fibres, on the other hand, the stabilization of a certain resistance or even their slight increase is possible.

Among the numerous existing methods of testing we have verified the tensile breaking strength, length, elongation, tear and burst resistance, folding endurance and stiffness.

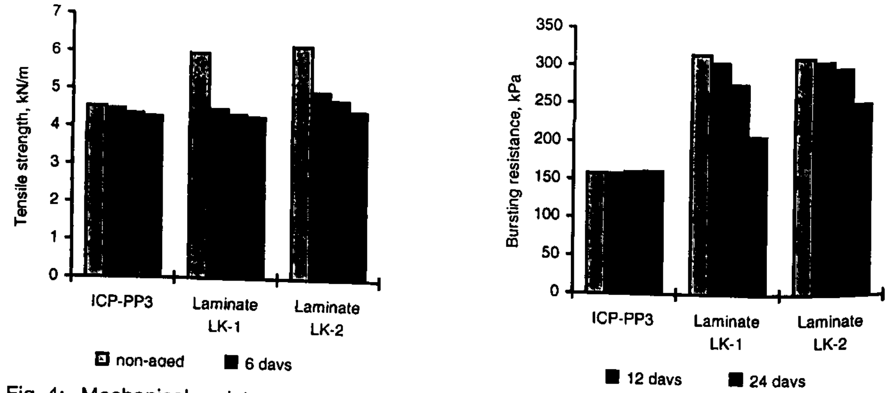

Fig. 4: Mechanical resistance: ageing effect on tensile strength changes in machine direction and on bursting resistance change.

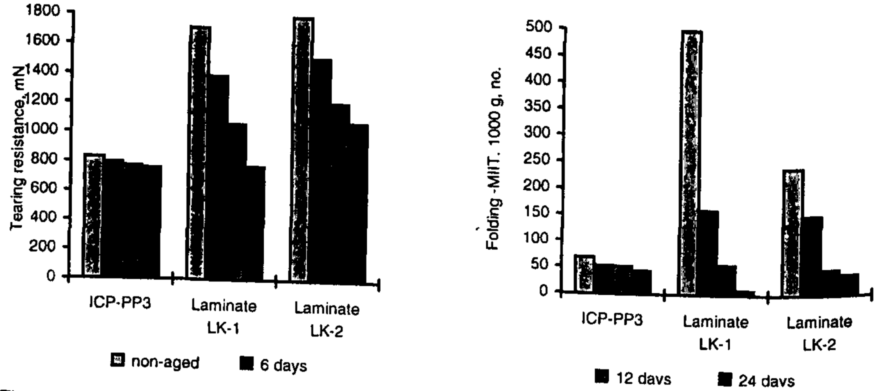

Fig. 5: Mechanical resistance: Decrease in tearing resistance and the number of double folding (MIT-1000gr method) on laminate samples composite on permanent paper sample.

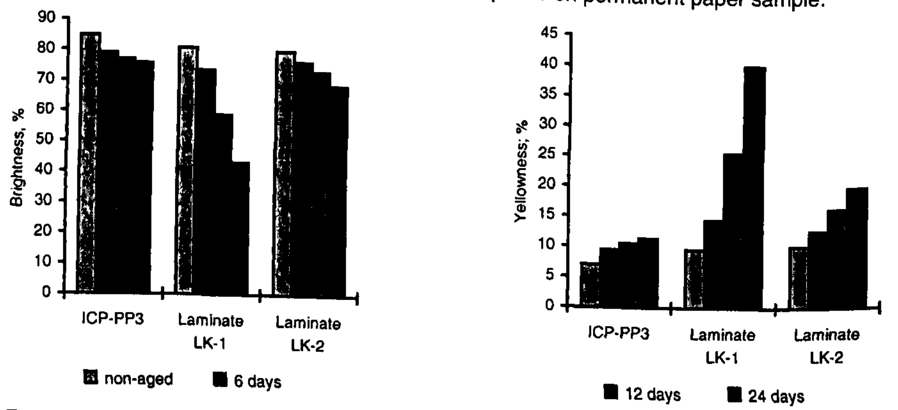

Fig. 6: Optical characteristics: Ageing effect on brightness decrease and on yellowness increase.

Tensile breaking strength, elongation, bursting resistance

Measurement results (Fig. 4) in all samples gave very high initial values in the laminate samples in comparison to paper, which, nevertheless, both diminish in time. The laminate LK-1 sample results were less favourable.

Tearing resistance, folding endurance and stiffness

As a rule, the tearing resistance of paper decreases with time. The test results given in Fig. 5 show that the tearing resistance in samples of the laminate composite was considerably lower (in sample LK-1 even more so), but we stated their remarkably high initial values in comparison to paper.

Cross-linking between cellulose chains and an increase of the cristallinity of polymer substances greatly influence the change of resistance to folding and stiffness of paper because the fibre-fibre link is strengthened.

The process of ageing greatly affects the considerable decrease of folding endurance capability and increase of stiffness and at the same time fragility. In both laminate samples the decline is even more noticeable in the laminate LK-1 sample. Paper, on the contrary, does not reach very high initial characteristics, but does not change substantially through ageing.

OPTICAL STABILITY

We did a follow-up on how the conditions of accelerated ageing of the chosen samples of paper and laminate composites influence the change of their optical characteristics, such as whiteness, brightness, yellowness, opacity, diffusion and absorption of light, using the Kubelka-Munk method.

Brightness, whiteness and yellowness

All samples, paper as well as the laminate composites, exhibited a deterioration of optical characteristics; cf. Fig. 6. Brightness and whiteness are not greatly affected in the paper and the laminate LK-2 samples, whereas these characteristics diminished greatly in the laminate LK-1 sample (by more than 50 %), so that the applicability for a final product (document) is highly questionable indeed. The same holds true for the values obtained for yellowness, which is greatly increased in the laminate LK-1 sample, whereupon the outer appearance of a document might be unacceptable.

The process of oxidative decomposition, especially of the low-molecular part of carbohydrates, results in the formation of carbonyl groups which greatly change with a decrease in brightness and whiteness, and increase in yellowness. This can result from a treatment with light or a treatment with raised temperature and relative atmospheric humidity (as in the case of accelerated ageing) without light. In this process new oxidation products are formed, which under adequate conditions even accelerate further decomposition and additionally deteriorate optical characteristics.

Metallic ions such as Cu, Mn and Fe cause an accelerated yellowing and deterioration of brightness and whiteness in cellulose fibres as well as in synthetic polymer materials. These ions are photo-catalytically active and have a high absorption in the UV region where they become reduced. They bring about a heightened photo-induced decomposition of carbohydrates. Metallic oxides and hydroxides catalyse the hydrolysis of a cellulose molecule even without the presence of acid substances. Such reactions are always irreversible – one-sided and furthered by an increased temperature.

Opacity, coefficient of scattering and absorption of light

In the process of accelerated ageing, opacity is increased in all the samples tested, paper, as well as the laminate composites , which should not be ascribed to light diffusion, but mostly to a large-scale increase of light absorption: An extremely great increase of opacity (connected with an optimum visual effect and non-transparency, respectively) was obtained in the laminate LK-1 sample, which was due

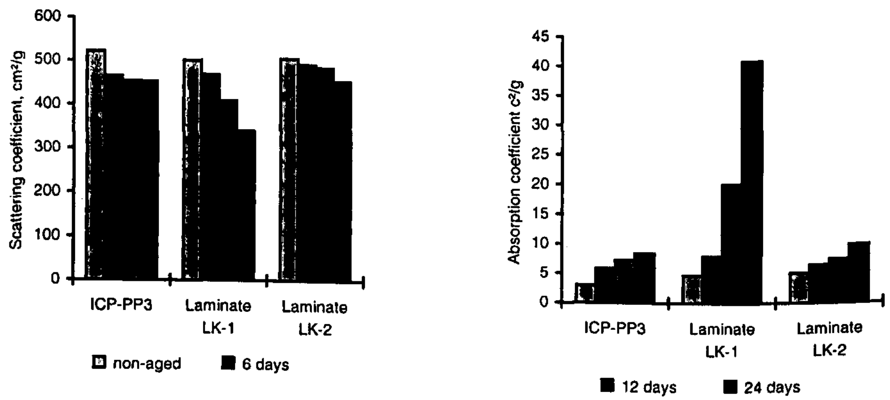

Fig. 7: Optical resistance: Effect of light scattering and light absorption on opacity changes.

only to a considerable increase of the light absorption coefficient. This is not recommendable for further application for material on paper to be restored or preserved, since the material becomes less resistant to external influences and is thus unsuitable to be used as a material of lasting value.

CONCLUSION AND FINAL RECOMMENDATIONS

The results of testing the chemical and surface stability, mechanical resistance and optical resistance of samples of laminated materials LK-1 and LK-2 on quality permanent paper ICP-PP3, using two different kinds of polymer foils, in the process of accelerated ageing according to ISO 5639/3 were as follows:

- The use of Filmoplast R for the permanent protection of materials used in the production of the laminate composite LK-2 is very suitable for the protection of documents. It obtains favourable results of chemical stability and good surface qualities; it is both mechanically and optically resistant, even when compared to the quality of permanent paper corresponding to ISO 9706 requirements.
- The use of PE polymer foil for the permanent protection of materials used in the production of the laminate composite LK-1 yields less favourable results with regard to permanence and durability and is unsuitable for protection over a long span of time. It shows a rather high degree of chemical instability, especially with regard to oxidation. The surface becomes increasingly hydrophilic and its mechanical resistance decreases, which is revealed in the lack of flexibility and bonding. Its visual aspect, defined by optical characteristics, deteriorates substantially.
- The conservation method of lamination and coating of documents and other materials on paper is very suitable both for protection and for saving extremely damaged materials, as well as for the rapid protection of great quantities of material.
- On the basis of the results of this research it can be stated that the use of more recent materials (Filmoplast R) is to be recommended since it assures a high degree of durability and permanence; a document is also thinner and the process of conservation more simple. Due to its rather high price, however, this latest method is to be recommended mostly for protection of very precious materials on paper.

The use of more permanent kinds of paper and other materials as well as the latest methods of conservation and preservation in preserving the cultural heritage on paper, for materials of lasting value is:

- indispensable for the preservation of one's heritage for posterity
- economically justified
- environmentally oriented.

SUMMARIES

Protection and conservation of materials on paper; evaluation of permanence and durability of the laminated material on paper

In the context of the two-year applicational research work in 1995–1996 entitled "Ageing of Paper and Board", the influence on quality of different types of paper as well as the different protection, conservation and restoration procedures on the durability and permanence of paper and printing and writing materials was researched. The project is performed at the Institute for Cellulose and Paper in collaboration of the National Archives, funded by the Ministry of Science and Technology and the Ministry of Culture of the Republic of Slovenia.

During the lamination as a conservation procedure we have stated the influence of different base materials (two kinds of polymer foils) on the end properties of a restored document. This was performed in comparison with permanent paper. The results of chemical stability, surface properties, mechanical strength and optical stability of paper and two kinds of laminates have shown the quality and usefulness of conservation procedures employing lamination. The research work has shown very favourable results of durability and permanence using the newest type of polymer foil material. Because of its high price it is recommended only for highly damaged documents and other printed and written materials.

Protection et conservation du papier; évaluation de la permanence et de la durabilité de papiers laminés

Dans le cadre d'un travail de recherche appliquée sur deux ans 1995-1996, intitulé „Vieillissement du papier et du carton" on a étudié l'influence de différentes sortes de papier, de différentes mesures de protection, de conservation et de restauration sur la permanence et la durée du papier et des documents imprimés et écrits.

Ce projet a été réalisé à l'Institut de la Cellulose et du Papier en collaboration avec les Archives Nationales; il a été financé par le Ministère des Sciences et Technologies ainsi que par le Ministère de la Culture de la République de Slovénie.

En observant le laminage, en tant que procédure de conservation, nous avons étudié l'influence des matériaux de base (deux sortes de lamelles de polymère) sur les propriétés finales du document restauré. Ceci a été réalisé en se servant de papier permanent comme modèle de référence. Les résultats obtenus quant à la stabilité chimique et optique, quant aux propriétés de la surface et à la résistance mécanique du papier au moyen de deux sortes de laminage ont mis en évidence la qualité et l'utilité de méthodes de restauration qui se servent du laminage. Les travaux de recherche ont donné des résultats très favorables sur la durabilité et la permanence du papier lorsqu'on utilise le dernier type de lamelle de polymère. Mais en raison de son prix fort élevé on ne le recommande que pour des objets gravement endommagés.

Schutz und Konservierung von Papier: Untersuchung der Haltbar- und Dauerhaftigkeit von laminierten Papieren

Im Rahmen eines Zwei-Jahres-Projektes (1995–96) der anwendungsorientierten Forschung mit dem Titel „Alterung von Papier und Pappe" wurde der Einfluß verschiedener Papierarten, verschiedener Maßnahmen zum Schutz, von Konservierungs- und Restaurierungsmaßnahmen auf die Dauerhaftig- und Haltbarkeit von Papier, auf Druck- und Schriftträger untersucht. Das Projekt wurde durchgeführt am Institut für Cellulose und Papier in Zusammenarbeit mit dem Nationalarchiv; es wurde finanziert vom Ministerium für Wissenschaft und Technologie der Republik Slowenien.

Bei der Beschäftigung mit dem Laminieren als eines Verfahrens der Konservierung untersuchten wir den Einfluß verschiedener Ausgangsmaterialien (zwei Arten von Laminierfolie) auf die langfristigen Eigenschaften von Papier. Als Referenz diente dauerhaftes Papier. Gemessen wurden die chemische sowie die optische Stabilität, Eigenschaften der Oberfläche und die mechanische Festigkeit zweier Laminate. Es zeigte sich, daß das Laminieren eine sinnvolle Restaurierungsmethode ist. Die Forschung erbrachte sehr günstige Ergebnisse hinsichtlich der Haltbar- und Dauerhaftigkeit des neuesten Typs von synthetischer Laminierfolie. Wegen ihres hohen Preises ist sie freilich nur für stark beschädigte Objekte zu empfehlen.

REFERENCES

1. Shahani, C.J., & R.E. McComb: *A clarification on specifications for archival paper.* Tappi Journal September 1987: 128.
2. Bansa, H.: *Messmethoden zur Bestimmung der Alterungsbeständigkeit von Papier,* Das Papier 1990: 481–491.
3. Waterhouse, J.F., & T.D. Barret: *The ageing characteristics of European handmade papers: 1400–1800.* Tappi Journal Oktober 1991: 207–212.
4. Hanecker, E., P.C. Le & R. Wilken: *Chemisch-physikalische Vorgänge und Eigenschaftsänderungen bei der Alterung von Papier,.* Wochenblatt für Papierfabrikation 1992: 521–528.
5. *International Standard for Permanent Paper.* Restaurator 14 (1993): 253–254.
6. ISO 9706 – Information and documentation – Paper for documents – *Requirements for permanence.* February 1994.
7. Klaubauf, H., & A. Proksch: *Die Forderungen der Nutzer von Papier an seine Alterungbeständigkeit und der Stand der internationalen und nationalen Normung.* Wochenblatt für Papierfabrikation 1993: 62–65.
8. Zeissler, P., U. Hamm & L. Göttsching: *Über den Zustand von Papier in Archiven und Bibliotheken.* Das Papier 1993: 62–73.
9. Frase, R. W., & J. I. Whiffin: *Preserving our documentary heritage the case for permanent paper,.* IFLA Section on Conservation 1996: 5–9.
10. Černič Letnar, M., G. Pepelnjak, G. Novak & J. Vodopivec: *Vpliv surovinske sestave in tehnoloških pogojev izdelave na staranje papirja (The influence of raw materials composition and technological conditions of production on the ageing of paper).* Papir 23 (1995): 58–64.

11. Černič Letnar, M., & J. Vodopivec: *Zaščita in konservacija gradiva na papirju – Vrednotenje trajnosti in obstojnosti* (*Protection and conservation of paper objects – evaluation of permanence and durability*). International Symposium of Book and Paper Conservation, Cekin Castle, Ljubljana, 3–5 July 1996.

Meta Černič Letnar, B.Sc., Researcher
Paper and Board Department, Institut za celulozo in papir
Bogišieva 8
SI-1000 Ljubljana
Slovenija.
Jedert Vodopivec, M.Sc.
Head of conservation and restoration department, Archives of the Republic of Slovenia,
Zvezdarska 1
SI-1000 Ljubljana
Slovenija

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Use of Chelating Agent EDTA with Sodium Thiosulphate and Sodium Borohydride in Bleaching Treatment

by JAAN LEHTARU & TULLIO ILOMETS

INTRODUCTION

The elimination of the chromophorically active substituent, a change in the chemical structure of chromophere by bleaching, is a widely discussed topic in conservation research. It is practically important to find less degradative bleaching methods, which have high bleaching efficiency and low colour reversion at the same time. Recently, tetrahydridoborates have often been used in conservation, because they raise the resistance of cellulose fibres to the acid hydrolysis, photo-oxidation, the effect of alkalis and ultraviolet radiation[1, 2, 3, 4, 5, 6].

Transition metals, such as iron or copper, catalyse the destruction of cellulose and participate in the foxing of paper. Transition metals can also cause decomposition of bleaches, which leads to the destruction of paper support. Consequently, it is very important to prevent transition metals from taking part in chemical reactions or eliminating them from paper. The use of chelating agents has been widely recommended[7, 8, 9].

In the present study we examined whether the complexing agent EDTA was capable of retarding the damaging effect of metal ions and whether it could be added to the reducing bleach. For this purpose a number of experiments was made: acid soluble Fe and Cu were measured and compared to the results obtained by using EDTA; brightness and colour reversion were observed and the content of carboxyl (COOH) carbonyl (CHO) groups were measured before and after the accelerated ageing of paper.

Materials and methods

Test paper

A rag paper: moisture content 3.62%, ash content 1.16%, content of extractives 0.01%. 19[th] century rag paper was manufactured in Russia and used for printing in Moscow (1832).

Bleach solutions

Seven different bleach solutions were used:

A 1% $NaBH_4$ (pH 9.5)

B 2% $Na_2S_2O_3 \cdot 5H_2O$ (pH 5.0)

C 2% $Na_2S_2O_3 \cdot 5H_2O$ (pH 9.5)

D 2% $Na_2S_2O_3 \cdot 5H_2O$ / 0.1 M EDTA (pH 5.0)

E 2% $Na_2S_2O_3 \cdot 5H_2O$ / 0.1 M EDTA (pH 9.5)

F solutions D (pH 5.0) + E (pH 9.5)

G solutions F + A

The procedures were carried out at room temperature (22°C) with less than 3°C variation among various treatments. Distilled water was used in preparation of all of the solutions. The pH was checked and adjusted to 5.0 and 9.5 with acetic acid or sodium hydroxide. Paper samples were bleached for four different times (2, 6, 14 and 26 min), using the same $NaBH_4$ solution. Borohydride solutions were not used immediately but allowed to equilibrate (by self buffering) 30 min, until hydrogen evolution had slowed down. After bleaching the samples were transferred to three different washing trays (with 1.5 l of distilled water) and washed for 10 min to remove residual chemicals. Paper was dried between acid-free blotters and after approximately 18 hours the reflectance was measured.

Brightness measuring was carried out using spectrophotometer fitted with an integrated sphere reflectance attachment using barium sulphate as a reference standard. The usual wavelength for the detection of yellowing of paper 457 nm was chosen.

Degradative effect was characterized by measuring carbonyl (CHO) and carboxyl (COOH) groups on paper. The content of aldehyde groups was determined by Copper Number (TAPPI Standard T 430) and the content of carboxyl groups by calcium acetate[10].

The accelerated ageing of paper was carried out during 28 days in darkness at 75°C and 40% of RH. After accelerated ageing brightness, the content of CHO and COOH groups were measured.

For the determination of iron and copper in paper a flame atomic absorption spectrometer (VARIAN Spectr AA 250 Plus) was used. Paper extracts were obtained by acid destruction according to SFS 3047 (Finnish Standard) and after treatment with $Na_2S_2O_3$/EDTA.

$Na_2S_2O_3$/EDTA method

A weighed sample of paper was placed in a 250 ml flask. 2% $Na_2S_2O_3 \cdot 5H_2O$ (50 ml) and 0.1 M EDTA (50 ml) was added. The sample was held in this solution for 14 min and then shaken for 3 min (22°C). pH was adjusted to 5 and 9.5 because ferric ions form the most stable complexes with EDTA at pH values from 4 to around 7 and copper around pH 8 to 11. The mixture was filtered and washed using two portions (50 ml each) of water and filtrate transferred to a 200 ml volumetric flask. For measuring Fe and Cu content with flame atomic absorption spectrometer 5 ml was taken.

The content of iron and copper

The average values of four measurements are presented in Table 1.

The iron content in paper extracts after treatment with 2% $Na_2S_2O_3 \cdot 5H_2O$ / 0.1 M EDTA (pH 5.0) makes ~1/3 of acid soluble iron content. The difference between copper content values is not considerable. It shows that EDTA works quite effectively.

Table 1. Iron and copper

	After treatment with acid	After treatment with $Na_2S_2O_3$ /EDTA
Fe	0.26 mg / 1 g paper	0.09 mg / 1 g paper
Cu	0.34 mg / 1 g paper	0.26 mg / 1 g paper

Results and discussion

Brightness values after bleaching

The datapoints for the average value for unbleached and aged samples are shown. The brightness of rag paper increases after washing from 81.07% to 88.68% (8.58% increase in brightness value compared to the initial value).

The bleach solutions may be listed in the following order of increase in brightness (Table 2, Fig. 1).

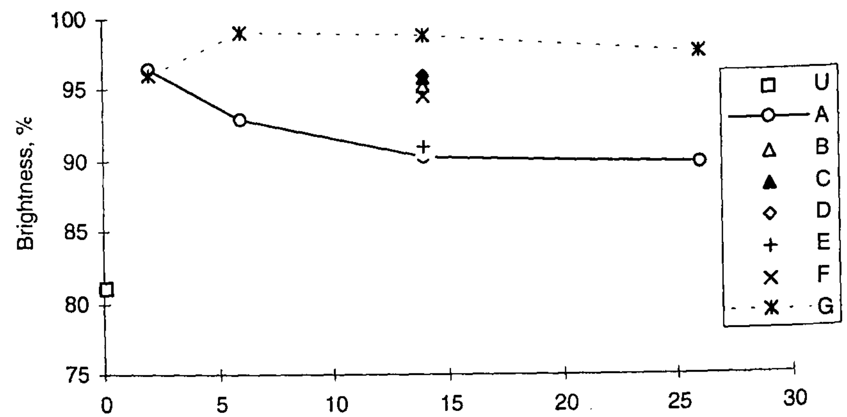

Fig. 1: Brightness of bleached samples (U = unbleached)

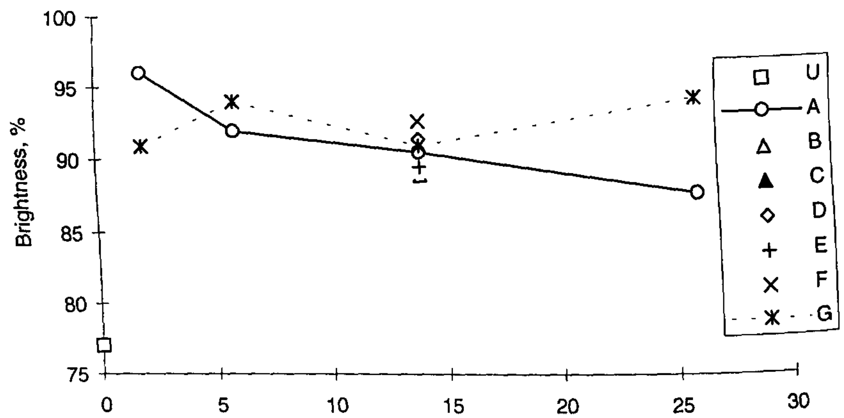

Fig. 2: Brightness of bleached paper after accelerated ageing (28 days)

The rate of colour reversion can be correlated to the total brightness change. Samples of paper treated with sodium borohydride solutions have a higher bleaching stability than those treated with sodium thiosulphate solutions. EDTA has no effect on the colour stability of paper treated with $NaBH_4$, but adding chelating agent to the $Na_2S_2O_3$ solutions seems useful (Table 3, Fig. 1 and 2). The washing procedure is very important, because washed unbleached paper shows a good brightness level after ageing when compared to an unwashed sample. All bleached samples have a higher brightness level after accelerated ageing than the unbleached sample before ageing (Table 4, Fig. 1 and 2).

Table 2: Results of measurements of brightness after 14 min of bleaching

Bleach solution	Brightness value after 14 min. bleaching (%)	Increase in brightness value after 14 min bleaching (%)
G	98.81	17.95
D	96.08	15.63
C	95.89	15.45
B	95.28	14.92
F	94.61	14.31
E	91.11	11.02
A	91.00	10.91

Table 3: Results of measurements of brightness after accelerated ageing (28 days)

Bleach solution	Brightness value after 14 min. bleaching (%)	Decrease in brightness value after accelerated ageing (%)
A	91.00	0.63
E	91.11	1.95
F	94.61	2.24
D	96.08	4.99
B	95.28	6.76
C	95.89	7.02
G	98.81	8.07

Table 4: Brightness, content of COOH and CHO groups

Bleaching		Brightness (%)		Content of COOH groups (x 10^{-3}%)		Content of CHO groups (Copper Number)	
Solution	Time (min.)	After bleaching	After ageing (28 days)	After bleaching	After ageing (28 days)	After bleaching	After ageing (28 days)
-	-	81.07	76.82	1.91	2.15	0.68	1.01
A	2	96.08	95.76	1.75	2.38	0.74	0.73
A	6	93.99	91.68	1.62	2.36	0.89	0.79
A	14	91.00	90.43	1.23	2.34	0.65	0.29
A	26	90.24	87.63	1.12	2.33	0.65	0.29
B	14	95.28	88.84	1.92	1.74	0.87	1.15
C	14	95.89	89.16	1.64	1.91	0.83	1.13
D	14	96.08	91.29	1.64	1.75	0.83	1.31
E	14	91.11	89.34	2.18	2.50	0.54	1.05
F	14	94.61	92.49	0.87	1.78	0.45	0.77
G	2	95.67	91.28	1.55	2.30	0.46	0.32
G	6	98.85	93.95	1.47	2.56	0.33	0.63
G	14	98.81	90.84	1.31	2.51	0.19	0.64
G	26	97.96	93.74	1.12	2.78	0.22	0.43

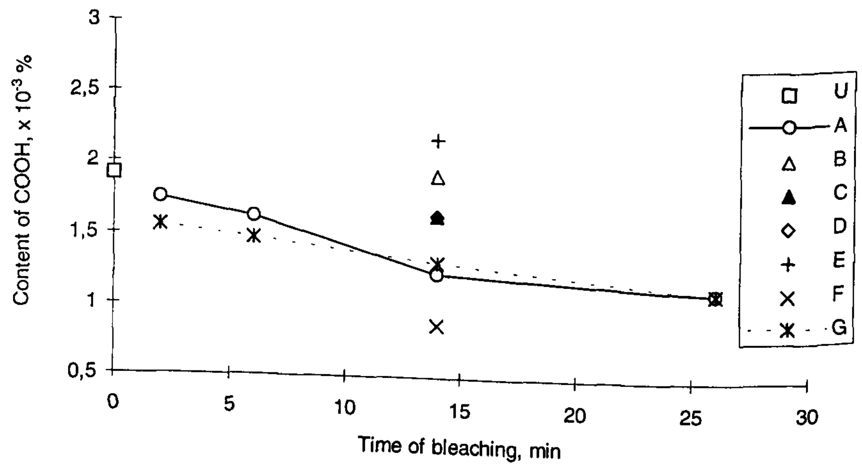

Fig. 3: Changes of COOH groups of paper after bleaching (U = untreated)

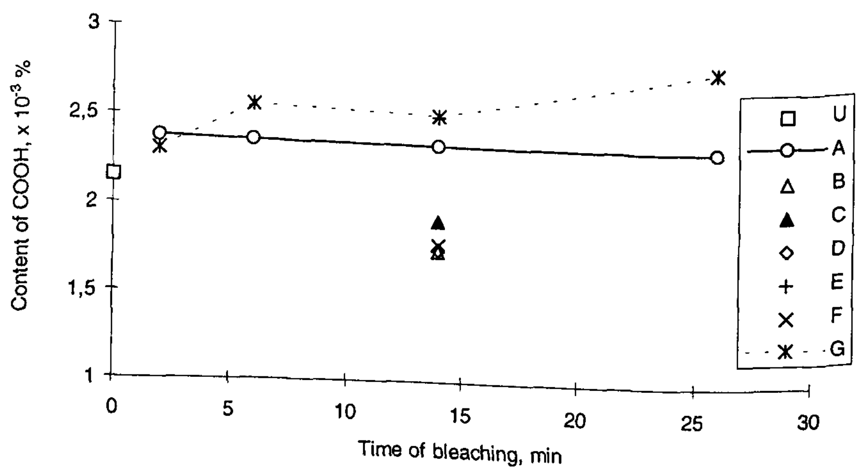

Fig. 4: Changes of COOH groups of bleached paper after accelerated ageing (28 days)

Changes in the content of carboxyl and carbonyl groups

Changes in the content of carboxyl groups using reducing bleaches are not remarkable. All bleach solutions (except solutions E and G) indicate a slight tendency to decrease in carboxyl groups after bleaching. The content of COOH groups in bleached samples after accelerated ageing is comparable to unbleached paper (Table 4, Fig. 3 and 4).

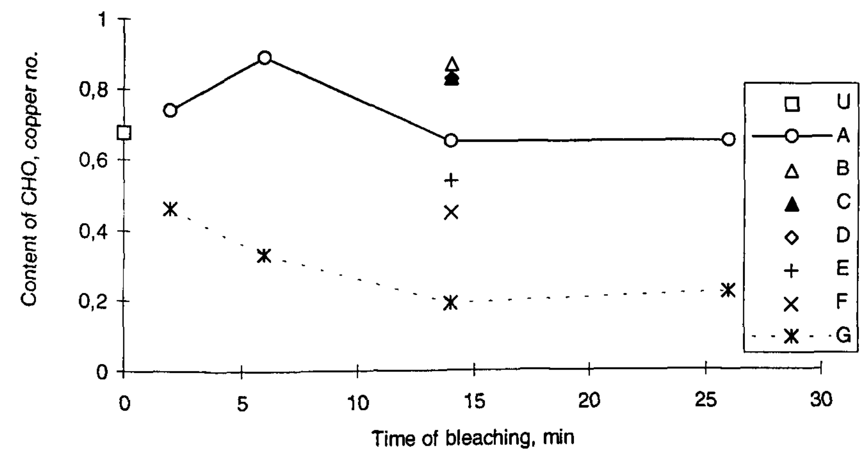

Fig. 5: Changes of CHO groups of paper after bleaching (U = untreated)

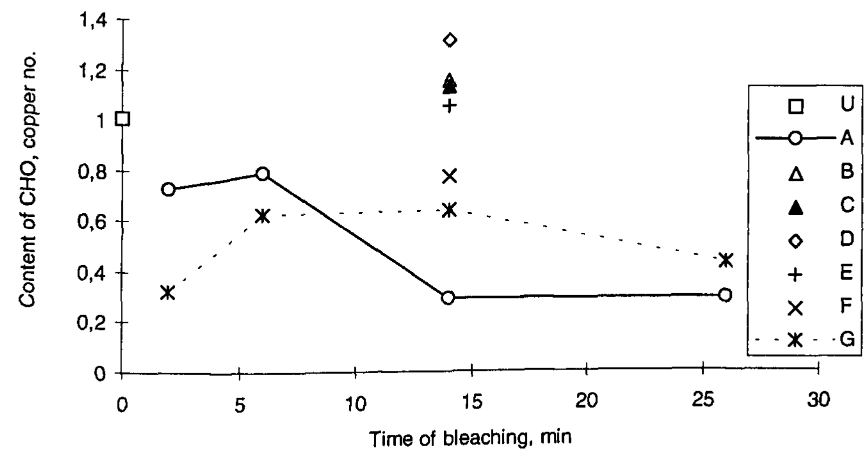

Fig. 6: Changes of CHO groups of bleached paper after accelerated ageing (28 days)

The biggest decrease in CHO groups was obtained by using bleach solution G (Fig. 5). It seems that the correlation to a certain extent between the content of CHO groups (which are responsible for yellowing) and brightness value does exist (Table 2, 3 and 4). Papers treated with bleach solutions A, F and G have a smaller content of CHO groups after accelerated ageing than unbleached paper (Table 4, Fig. 5 and 6).

CONCLUSIONS

- Chelating agent EDTA can be shown to be useful in the removal of iron and copper on cellulose fibres. The best approach to the removal of stains caused by iron and copper is the use of a reducing agent coupled with a chelating agent.
- EDTA improves the colour stability of papers treated with sodium thiosulphate, but does not benefit to the colour stability of paper treated with $NaBH_4$.
- Supposedly, Fe and Cu ions, which remained in paper, were released from the complexes by chelating agent, they can be oxidized and the preliminary effect of EDTA is lessening in the course of time.
- Despite of the lower content of CHO groups after bleaching, the paper samples treated with EDTA indicate the tendency of CHO content to increase after accelerated ageing.
- It is necessary to introduce Mg and Ca ions back into the paper after treatment with EDTA.
- The use of EDTA in practical conservation is limited owing to it stimulating the adverse effect of ink corrosion.
- The mechanism of all reactions which take place in paper when EDTA is used as a chelating agent are still not clear and need more detailed investigations.

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SUMMARIES

Use of chelating agent EDTA with sodium thiosulphate and sodium borohydride in bleaching treatment

This article briefly reviews the use of chelating agent EDTA with sodium thiosulphate and sodium borohydride in bleaching treatment. A rag paper (1832) was chosen for experiments. Acid soluble iron and copper were measured and compared to the results obtained by using EDTA. Brightness and colour reversion were observed and the content of COOH and CHO groups were measured before and after the accelerated ageing of paper. It is shown that the chelating agent can be useful in the removal of iron and copper on cellulose fibres. The best approach seems to be the use of a reducing agent coupled with a chelating agent. If sodium thiosulphate is used the

colour stability of the treated paper is improved, but this is not the case with $NaBH_4$. Altogether, the mechanisms of all reactions which take place in paper when EDTA is used are still not clear and need more detailed investigations.

Utilisation de l'agent chélateur EDTA au thiosulfate de sodium et au borohydrure de sodium lors du blanchiment du papier

L'article décrit brièvement l'utilisation de l'agent chélateur EDTA au thiosulfate de sodium et au borohydrure de sodium dans la procédure de blanchiment du papier. Le papier retenu pour nos analyses est du papier chiffon datant de 1832. Les mesures suivantes ont été effectuées: teneur en fer et en cuivre par la méthode acide, blancheur et stabilité de la blancheur, teneur des groupes COOH- et CHO avant et après le vieillissement accéléré. On démontre que l'agent chélateur peut être utile pour éliminer le fer et le cuivre des fibres de cellulose. La meilleure approche semble consister en l'utilisation d'un agent réducteur couplé avec un agent chélateur.

Les résultats des recherches ont démontré que l'utilisation des agents chélatiques (EDTA) avec l'agent réducteur est efficace pour la séparation du fer et du cuivre du papier. Avec l'utilisation du thiosulfate de sodium, la stabilité de blancheur des papier s'est améliorée, sauf pour le papier traité par $NaBH_4$. En général, le méchanisme des réactions en présence de EDTA n'est pas suffisamment clair et demande de recherches supplémentaires dans l'avenir.

Die Anwendung der Komplexverbindung EDTA beim Bleichen zusammen mit Natriumthiosulfat und Natriumborhydrid

Der Artikel gibt einen Überblick über die Anwendung der Komplexverbindung EDTA beim Bleichen zusammen mit Natriumthiosulfat und Natriumborhydrid. Für die Untersuchung wurde Hadernpapier eines Buches aus dem Jahre 1832 verwendet. Es wurden folgende Messungen durchgeführt: Säurelösliches Eisen und Kupfer, Weißgrad und Farbstabilität, Gehalt von COOH- und CHO-Gruppen vor und nach der künstlichen Alterung. Es wird gezeigt, daß der Chelatbildner nützlich sein kann zum Entfernen von Eisen und Kupfer aus Cellulosefasern. Die beste Wirkung scheint die Kombination eins Reduktionsmittel mit dem Chelatbildner zu sein. Hierbei verbessert Natriumthiosulfat die Farbstabilität des behandelten Papiers, nicht aber Natriumborhydrid. Insgesamt sind die Ablaufmechanismen und die Reaktionen, die beim Einsatz von EDTA stattfinden, nicht völlig klar und bedürfen weiterführender Forschung.

REFERENCES

1. Durovic, M.& J. Zelinger: *Chemical processes in the bleaching of paper in library and archival collections.* Restaurator 14 (1993): 78–101.
2. Burgess, H.: *Practical considerations for conservation bleaching.* J. IIC-CG 13 (1988): 11–26.
3. Hey, M.: *Paper bleaching: It's simple chemistry and working procedures.* Paper Conservator 4 (1979): 10–23.

4. Burgess, H.: *The colour reversion of paper after bleaching.* Conservation of Library and Archives Materials and the Graphic Arts. G. Petherbridge, ed., London: Butterworth 1987: 328.
5. Lienardy, A., & P. Van Damme: *A bibliographical survey of the bleaching of paper.* Restaurator 9 (1988): 178–198.
6. Sobucki, W.: *Borhydride - wertvolle Mittel zur Restaurierung von Papier.* Restauro 1993: 260–263.
7. Cotton, F. A., & G. Wilkinson: *Advanced inorganic chemistry.* Xxx: Wiley 1988: 1455.
8. Kask, U. & J.D. Rawn: *General chemistry.* Xxx: WCB Communications 1993: 988.
9. Salomons, W., U. Förstner & P. Mader: *Heavy metals.* Heidelberg: Springer 1995: 412.
10. Lehtaru, J.: *Changes of content of carboxyl groups on different kinds of paper during accelerated ageing.* Acta et Commentationes Universitatis Tartuensis 966. Publications on Chemistry XXI. Tartu 1993: 197–210.

Jaan Lehtaru
Tartu University Library
1 W. Struve St.
Tartu EE2400
Estonia

Tullio Ilomets
Institute of Organic Chemistry,
University of Tartu
2 Jakobi St.
Tartu EE2400
Estonia

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Preservation of Collections at the Russian Academy of Sciences Library

A Retrospective Overview, Problems and Solutions

by JULIA P. NYUKSHA & VALERII P. LEONOV

INTRODUCTION

The Library of the Russian Academy of Sciences (Biblioteka Rossijskoj Akademii Nauk; BAN) was founded by Peter the Great in 1714. Its core was formed by the materials which the Emperor has collected travelling abroad, and which thus have become the property of the royal family. The library gained recognition as an international scientific centre in 1725. Today its unique collections comprise 20 million books on science, fine arts, and culture of different epochs; many of the books (for example the Radzivill Chronicle) are cultural monuments of world importance.

Nowadays the BAN is the largest academic library in the world, and a major research centre. Over 3,000 foreign libraries and information services participate in literature exchange programs with the BAN[1].

THE FIRE

On February 14–15, 1988 a devastating fire, the largest in the century, took place at the BAN. Over 400,000 books have been destroyed by the fire, and about 3.6 million have been damaged, including the famous Baer collection, named after the German scientist Karl Baer, who performed the cataloguing of the library's foreign books collection at the 19th century[2].

The fire at the BAN was extremely disastrous (Fig.1), nevertheless the very next day the fire recovery efforts were started and the control over the situation was regained, thanks to the support of the City Administration, the St. Petersburg Branch of the Academy of Sciences and many institutions. Joint efforts of scientists, who formed a special interagency experts' group, enabled to organize regular work in various directions[3]. Besides that, many international institutions like the

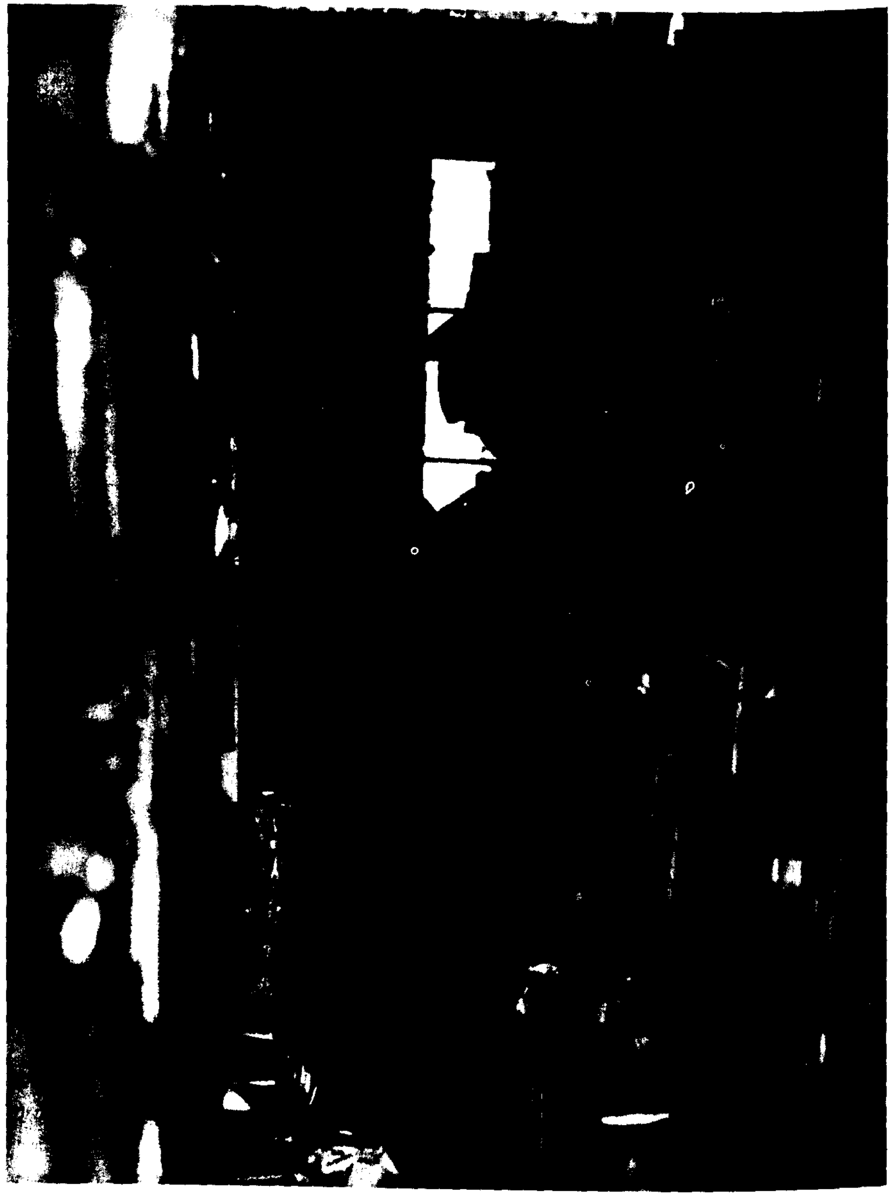

Fig.1: The repositories after the fire

Foundation for Survival and Development of Humanity, UNESCO, the International Council of Archives, the International Federation of Library Associations, the Library of Congress, as well as private businesses, responded to the disaster

offering their assistance[4]. A vast field of activities was opened for conservation specialists of the BAN and the other libraries and archives of St. Petersburg.

A major feature of the conservators' actions in a disaster is that all operations and treatments, even the most trivial ones, have to be performed over a large number of items and in a very short time. Hence the search for the methods of massive conservation, some of which are invented "on the fly", so as not to lose the precious time necessary to save collections. Thus it was in 1988, during the recovery from the disastrous BAN fire. For the conservators it was a crucial period when many things had to be reconsidered and reassessed. The authors of this articles venture to offer their ideas, views, experience and innovations, principles and concepts that arose in connection with the fire.

FIRE RECOVERY

The fire recovery efforts developed in three main directions.

- First, it was necessary to mobilize all the techniques and technological means known to be used under normal circumstances. In shortest time possible they have been modified and applied in the emergency caused by the fire.
- Second, due to the scale of the disaster, a new system of temporary stage-by-stage treatments had been developed, which laid foundation for a regular plan of collections recovery.
- Third, the fire has made apparent the need of innovative original developments for which there had been little demand before.

Of the first group of measures it may be of interest to mention the significant improvement of the drying techniques for the books that have gone totally wet, and the implementation of large-scale disinfection of repositories and books, which, because of the over-moistening of the repositories were facing the risk of a massive fungi attack, detrimental for both people and books.

In the course of fire-fighting hundreds of tons of water have flooded 22 repositories of the BAN. Six tiers of the repositories, with total volume of 24,000 cubic meters have been affected by water and steam. In these facilities over 6.8 million imprints were stored.

DRYING TECHNIQUES

In the circumstances of such a disaster huge efforts were made to mobilize the resources so as to speed up the drying process, employing all known techniques, including freezing. In particular, diffusive drying, commonly used in conservation practice, was applied. This technique consists in drawing the water off the wet book block by means of filter paper or another material with good hygroscopic properties. The drying of separate sheets was performed using heated surfaces of various devices, like platen dryers, photographic print dryers, and the like. The books were exposed to leaf drying in a flow of warm air, the speed of which was being changed at a certain rate. This was reached using various electric convectors, dryers, fans, and other devices. All of these methods are not quite satisfactory, and it is not just for the reason of being time-, and labour-consuming. Employing them always leads to complex deformation of various parts of book materials. Drying in high-frequency magnetic field proves to be much more effective in this respect, though it has drawbacks of its own, especially when applied to charred materials. Sublimation and vacuum drying, or their combination, have generally accepted advantages.

AERODYNAMIC DRYING SYSTEM

The library had a high-frequency device, but it did not possess the equipment for sublimation drying, which is most suitable for drying frozen books. However, a decision to this problem was soon found, without resorting to the use of complex equipment. While the work was already in progress, an aerodynamic system was developed in a very short time, enabling to dry the frozen books without unfreezing them, while leaving the books well retained. Blocks of frozen books were packed into moisture-absorbing, mattress-type, sawdust-filled wrappers. The blocks thus packed were freely placed on open shelves in a spacious chamber. About them strong closed flows of hot air were created. The air streams pierced the blocks with books and also circulated around the perimeter of the drying chamber walls. A separate powerful fan discharged the humid air out of the chamber. At the same time dry air was sucked in.

The process ensured gradual dehydration of the books packed into blocks without any deformation or deterioration of the materials. The state of the materials was controlled thermometrically, hygrometrically, and by means of selective assessment of the mechanical properties of paper. The drying continued until an equilibrium moisture content corresponding to that existing in normal storage conditions was reached, with relative humidity of $55\% \pm 5$, and temperature of $18\,^{\circ}C \pm 2$. The speed of dehydration depended on the rate of motion of the air flows and the composition of the sawdust used as adsorbent. The rate of unfreezing was within $0.4\,^{\circ}C \pm 0.1$/min and also depended on the structure and composition of the books. At the beginning of the process the air temperature decreased whereas the block temperature increased. It is only after the equilibrium of the temperature in the air and within the book blocks had been reached, that the rate of air flow was reduced to a temperature gradient of $0.15\,^{\circ}C \pm 0.05$/min. The process continued until the ambient temperature reached $18\,^{\circ}C \pm 2$. This took 8 ± 2 hours.

After the drying had been completed, a process of stabilization began in the materials. The packing wrappers were taken off and the books were removed from the chamber. Then they were stacked for subsequent disinfection and rehabilitation, under permanent control[4].

Over 150,000 books have been dried this way, without the slightest damage to, or deformation of paper and bindings. The drying system used at the BAN was a significant technological improvement and even has some advantages over vacuum sublimation drying in special chambers. This technology ensures uniform drying of books, and at the same time makes for maintaining a prescribed humidity level in them throughout the entire drying cycle. Besides, the advantage of the method over vacuum drying is that drying will not come until the pressure reached in the material have caused corresponding strains in it, under permanent humidity control. It also should be mentioned, that there is no way to control moisture contents in books while sublimation drying is in progress.

THREAT OF MOULD GROWTH

Despite all the measures taken in order to hasten the drying, there was an imminent threat of mould growth in many places of the multi-deck repositories. In 10 days contamination of the air has increased three times. The high content of viable fungal diaspores equally dangerous to books and people caused serious concern. Among the fungi potentially pathogenic representatives of the genus *Aspergillus* were predominant, among them *A. flavus*, *A. fumigatus*, *A. versicolor*, *A. terreus*, *A. niger*, and some others. The ubiquitous fungi of the genera *Rhizopus*, *Mortierella*, *Mucor*, *Cunningamella*, with their enormous reproduction capacity at high humidity, which reached 100%, also contaminated the environment with their spores. It is well known from medical mycology that under certain conditions they can cause human mycoses, which are not localized geographically. Fungi of the genera *Alternaria*, *Acremonium*, *Cladosporium*, *Scopulariopsis* which are permanently found on damaged bindings and paper, because of the significant environment contamination and concentration of people working with the books, heavy work of the drying devices, which spread the diaspores, gained favourable environment for getting onto people's skin, hair, nails, clothes, which has been reliably proved, pose a health hazard.

DISINFECTION

Having analyzed all the available city resources and taken into account the urgency and possibility of performing work in close proximity of the inhabited buildings, the commission of experts took an unambigous decision to consider disinfection of the repositories as an immediate priority in the fire recovery efforts[5].

During the period form April 19, till May 27, 1988, 8.1 mill. volumes underwent disinfection right on the shelves of the repositories. The disinfection technique employed in this case was to a considerable extent different from all the procedures known so far. The plan was to perform massive decontamination of the hermetically sealed repositories, together with the books located in them, by means of aerosol fumigation, which would produce no detrimental effect on people and books. In case the traditional chamber techniques were used, this work would have taken no less than 2 years.

PROCEDURE

The procedure was as follows. All windows, doors, and slits in the repositories were hermetically sealed. Within the rooms a series of ventilating devices ensured an aerodynamically closed ring. The rooms were preliminarily warmed up using electric fans; in addition the environment was moistened. The temperature was set to 40°C±5. This hot and humid environment in 1.5–2 days triggered the growth of fungi spores, which in the form of vegetative *mycelium* are more sensitive to physico-chemical impact. This made it possible to limit the contents of formic aldehyde in disinfection composition to 40 grams per cubic meter of the room, and thus to alleviate the mode of operation.

The disinfecting agent was a composition, including 8% formic aldehyde, 40% carbon dioxide and 52% water. The composition was introduced into the repositories environment using ultrasonic nozzles. The aerosol mixture got into the closed convective heat gas flows and in a short time spread over the whole room.

The exposure continued for 1 to 10 days, with permanent mycological control of the books and storage rooms environment. One day after the composition mixture had been introduced, the contamination of the books was reduced by the factor of 10–15, and on the tenth day, by the factor of 75. The process was stopped, when the treatment efficiency reached 95–100% against the initial content of the diaspores in the air and on the books[6].

Upon completion of the disinfection, the formic aldehyde was neutralized by an equimolecular amount of ammonia, with gas flow passing from the room via the sorption filters installed on the exhaust window fans.

Contamination or leakage of the disinfecting agent into the environment was precluded due to the exact calculation of the parameters of the production process. All cycles of the disinfection treatment were performed under permanent control of the city's sanitary and toxicological authorities. This resulted in satisfactory, rapid, and ecologically safe prevention of a massive fungi attack on vast book collections, stored closely to the repositories that were damaged during the fire. The library's staff and volunteers were reliably safeguarded against the mycological diseases.

NEW PERCEPTIONS

The BAN disaster can be compared to losses suffered in the Florence flood of 1966 and in the Los Angeles Public Library fire of 1986. Both cases required maximum exertion of efforts and a search for non-standard solutions. There also was an unquestionable similarity in that valuable cultural heritage were among the items that have suffered damage. Many items damaged in the BAN fire should be by all means preserved per se. Of the 518,000 imprints of the Baer Collection 180,000 were carried away by the fire of 1988. The others were damaged by the fire, and they had to be preserved at all costs[2].

As it nearly always happens in disasters, the fire recovery program at BAN was based in many respects on the well-known and tested techniques. However, what has been said before is not an exception to the rules: the work revealed radical innovations, including those so significant that they are worthy of recognition and are a valuable contribution to the development of conservation. They certainly include mass disinfection of the repositores and drying of the frozen books.

At the same time it has become evident that a part of the issues brought about by the disaster requires deeper and more considered study; and that they can not be resolved on a short time frame of the current work. Without having radical means available it was yet necessary, one way or another, to save the damaged copies from the inevitable subsequent disintegration. This objective was best answered by the concept of "preventive conservation".

PREVENTIVE CONSERVATION

The program of preventive preservation is a program of temporary, stage-by-stage, step-by-step treatments, sufficiently quick, and performed over a large number of imprints. Materials must, to a maximum possible extent, be preserved, and their possible subsequent disintegration prevented, care being taken to observe the rules of usual library shelf storage. Concurrently with these temporary steps, fundamental research should be carried out along with the search for new unusual solutions and the development of new original techniques. In other words, it is only after the reliable new technologies, guaranteeing long-term preservation, have been found, they may gradually without undue risk and haste, be applied to the imprints being in a state of temporary conservation.

Such formulation of the problem meets the goals of scientific conservation the best way. And it was taken as the main idea, the concept of the works performed in order to ensure preservation of the BAN collection after the fire.

If, in these circumstances, one considers the general idea of conservation in all of its scope and in its relations with various directions of activity in the field of preservation of the library collections, than these latter could be assumed as its components. Much like the idea of preventive conservation, it has grown into library ideology, implying variability of the sets of measures and methods applied towards imprints and manuscripts in different periods of collection existence.

THE PHILOSOPHY

The philosophy of preventive conservation is developed by the Getty Conservation Institute and the Library of Congress (USA). It can be characterized by the following concepts and is developed in several directions[7].

The concept is based on the indisputable truth that the time of existence of all organic materials, which form the material substrate of a book, is limited, and that they cannot be preserved forever. Ensuring their preservation, even with serious scientific prerequisites, and skillful mastery cannot prevent, but can only for a more or less extended time retard the onset, the inevitable moment of the complete disintegration of an original.

It this connection, as the concept has it, it is necessary to carefully protect the book materials from unjustified (from the point of view of future preservation) restoration treatments, which are potentially capable of becoming one of the factors intensifying disintegration of paper and books. For all their uselessness, and, in the final analysis, even harmfulness, these treatments also require tremendous expenditure.

This economic side of the issue is not unimportant. It is all the more significant in that it enables to redirect the efforts towards research and precise interpretation of the process of damage of library materials, bringing them to a level of new refined understanding, which would enable to create long-term programs on this basis.

This is the way to follow in order to assure the emergence of new, more thought-out solution in the field of conservation in contrast to rash immediate

actions with a short-term effect, which do not warrant long-term storage of documents in libraries.

These principles, having been integrated into a unified system and re-interpreted in accordance with the BAN conditions, now form an integral ideology of conservation, which is applied in a given library. There is also no doubt that the adopted concept of conservation requires, as it is being developed, the development of new principles and means of ensuring preservation of documents in libraries. Its implementation requires the solution of a number of scientific, practical and technical problems. This system of preservation is based on radically new approaches. It is established on a complex of preventive measures which to a large extent are new and have not earlier been used in libraries.

NORMATIVE PRESERVATION

The practice of conservation is in large measure aimed at providing various mechanisms for the prediction of processes occurring in the materials of imprints and manuscripts as they are permanently stored in the library repositories. This assumes their permanent stay in repositories, where they are subjected to complex impacts due to changes in the condition of the buildings, utilities, and the environment.

The purpose of collection preservation at the BAN is to track the possibility of such changes and to adjust them technically, so that the normative preservation of the imprints could be observed. One of the most complex issues within this framework is to elaborate an integral measure that would characterize the normative condition of preservation for the entire complex of materials constituting an edition. For this purpose it is first of all necessary to perform primary definition of normative preservation of every material with subsequent computer processing of the data in the search for an optimal set of parameters, such that there will be minimal changes in each of the materials.

In connection with this formulation of the non-conventional problems, many questions have arisen. For example, the question of separate storage of bindings and book blocks, because the optimal storage conditions for either of them are different. In practice, preference is always given to information carriers, and, in large measure, to the most widespread of them, the paper. It is possible that there will arise the necessity to divide the collection not by subjects or chronologically, but by the chemical composition and properties of different materials. This is established practice for paper and microfilm collections.

Deepening of the ideology and the renewal of the essentials and techniques of conservation will in perspective lead to a change in the routine library practice which has not until now been put into conformance with the requirements of normative preservation, but has followed other principles. A certainly important direction in the development of this idea is the change in requirements for the polygraphic production, which would result in compatibility (in terms of preservation) of the materials, used in manufacturing of polygraphic products. And, still deeper, the choice of the materials used in polygraphy for producing editions with different life cycle and different usage form.

The immediate task of preventive conservation is to elaborate the system of parameters and a program which would enable to monitor the change of each of the component for each of the materials in conditions, normative for the latter and normative for other materials. In the final analysis conservation implies integration in one system and coordinated use of all knowledge accumulated on each imprint and manuscript, for working out rational norms that would take into account techniques used in the production of the document, form of its storage, conservation and library routines. Such formulation of the problem brings one to the idea of the need for new education of librarians so that they could become aware of the needs of normative preservation and provide conditions for it. The librarians ensure the overall success here. They should participate in the conservators' work on developing new forms of library technologies.

The Baer Collection, which required immediate recovery measures because of the damage caused by the fire, became the starting point for the implementation of conservation program at the BAN. The damage that the fire inflicted upon the Baer collection, has taken the form of either complete destruction of imprints, or a partial change of their physico-chemical properties, partly caused by fire-fighting.

PHASED CONSERVATION

Since the very beginning of the tragic events down to the present time the BAN has been receiving help from the world community in various forms and from various establishments, such as cultural institutions and businesses from different countries. The BAN was visited by Peter Waters, Sally Buchanan, Carolyn Sung, Frank Preusser, Jane Siena, Ken Harris, Irina Averkieff, Donald Etherington, and others. These experts from the Library of Congress, the Getty Conservation Institute, and other institutions, having evaluated the situation, suggested a technique of partial, stage-by-stage "phased conservation" used in American libraries. Its main idea is to prevent further deterioration of imprints and ensure their sustained preservation by means of putting them into microclimatic containers (Fig. 2). It is also important, that these measures improve the environmental condition in repositories.

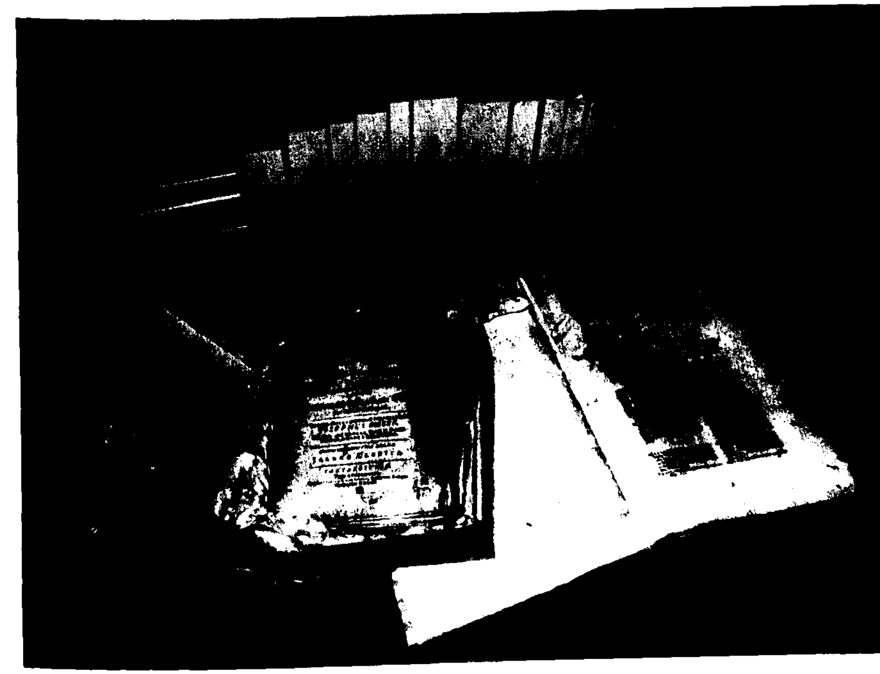

Fig. 2: The books in phase boxes

The BAN specialists, together with American experts, drew up a program of "phased conservation". Using a custom container for every non-standard sized book turned out to be uneasy and laborious business.

It has to be mentioned, that this idea was successfully tested in the library practice of the past. As far back as 1944, after lifting of the fascist blockade, many imprints of the Russian National Library and other libraries of the city were in a grievous state. All of them, after disinfection treatment, were put into dense wrappers made of kraft paper. In this form they were stored for a long time and without any damage, awaiting their turn for stabilization and restoration. At the post-fire BAN the work was performed at a higher level, corresponding to the present-day scientific and technical potential. Various types of double-faced corrugating acid-free board were used to produce containers, quite advanced in design, using computer technology.

The collection destined for boxing was divided into two parts (turns). The first turn comprised the most valuable collections of the 17th–18th centuries. A system was developed for compiling of an automated database, in which the data on the history and composition of the collection, as well as on over 50 parameters, describing preservation condition, the degree of damage, physico-chemical and biological characteristics, are being accumulated. A program has also been developed

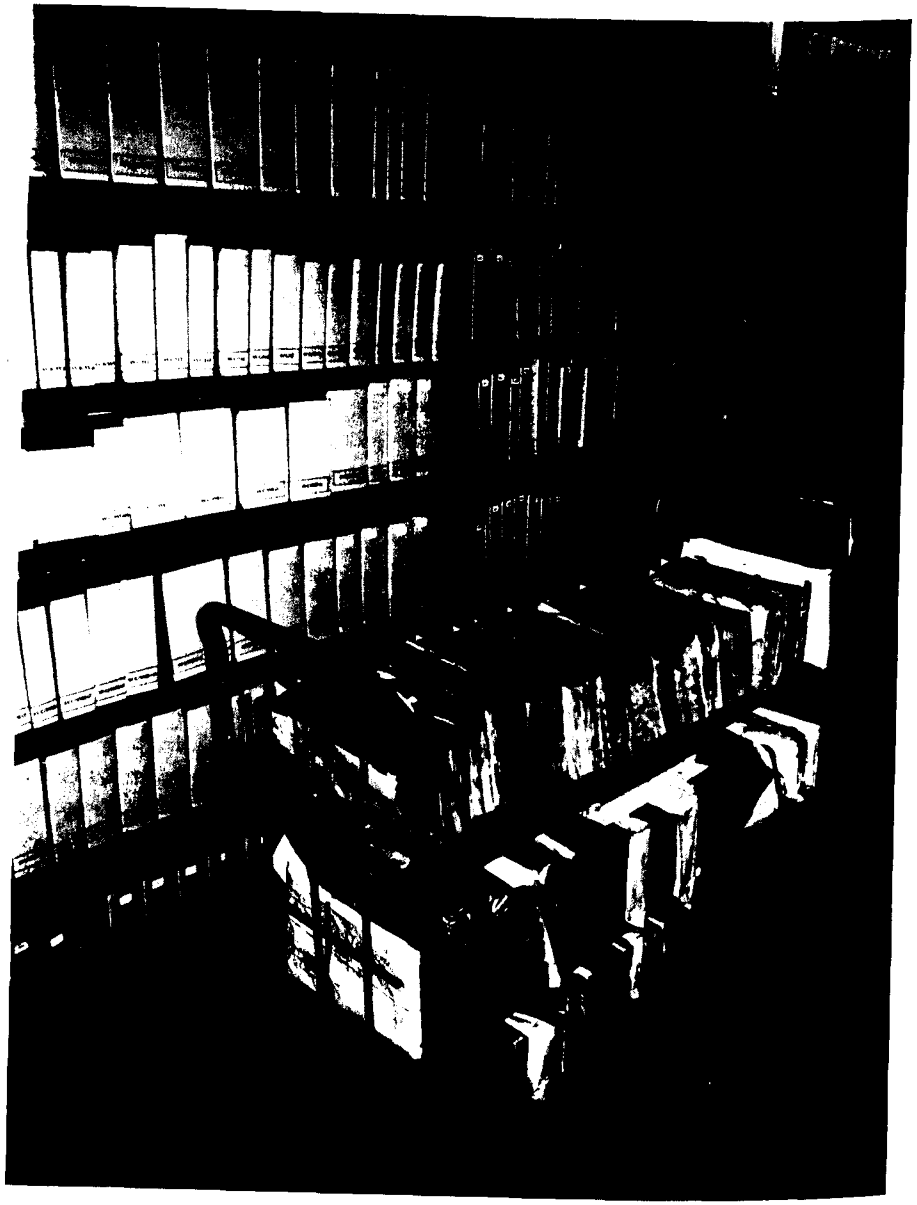

Fig. 3: The phase boxes shalving in the repository

to monitor the condition of the collection. The database has started accumulating the data on changes in the parameters characterizing the preservation condition of the materials that form the substrate of the books[8]. Besides that, the database

enables to compare the state of the books, stored the usual way, and the books enclosed in microclimatic boxes.

By the present time 28,000 books of the Baer Collection have been put into boxes (Fig. 3), which were made using the US equipment. In collaboration with the All-Russian Institute for Paper the BAN specialists have performed much research on developing the technology which would enable to manufacture the board used in making boxes at enterprises of the Russian paper industry. An experimental batch of such board has been successfully tested. This work is now being continued, with the goal to produce the boxes for another 40,000 imprints. Thus, a special technology, information and monitoring system, providing for the preservation of the books of the collection, have been developed and now are being implemented. Besides, the program is planned to be further developed, so that the phased conservation technology could be used in preservation of collections of great cultural and historical value.

CONTAMINATION BY WATER IMPURITIES AND POLLUTION

The next direction of the work consists in performing a new type of intensive investigations. The need for them is based on the specific conditions that have formed at the BAN after the fire, and which are related with especially unfavourable factors. Due to this, the properties of the imprints which underwent the fire have deteriorated considerably, so their recovery will require non-conventional methods. It is only when such methods become available will it be possible to define new technological cycles. This, in large measure, applies to deacidification technology.

An extremely important factor in resolving this problem is the pollution of water in St. Petersburg. The fire was extinguished using water drawn directly form the Neva, which is greatly polluted[9]. It is sufficient to mention many substances of organic origin, such as petroleum residue, acetone, ethyl acetate, benzol, butanol, toluene, and others. This water includes practically all metals in different concentrations, but especially significant is the presence of zinc, copper, nickel, manganese, and, most of all, iron, the quantity of which amounts to 300 µg/l. This being the case, the metals occur in the form of salts of various acids. Especially abundant are nitrates, nitrites, chlorides, sulfates, and others. Humin acids are present in great amount. It should also be remembered that as the water was drawn, components of bottom sedimentation could find their ways into the repositories. Besides, in accordance with the fire-fighting practice, the water was mixed with detergent-type foamers, which constituted 3–4 % of its volume. For hours many fire engines poured this mixture onto the books in tremendous amounts, considering the fact that one engine alone delivers 0.5 t. water per second.

Thus, one can say without exaggeration that the books which had been impregnated with solutions of complex chemical origin, while being dried, were enriched with a non-controllable mixture of compounds of various chemical nature. These materials, the composition of which has significantly changed, should be subjected to stabilization and restoration. Doubtless, one may assume that the technological process of their restoration should be different form those accepted or usual books that are subjected to natural ageing. Moreover, the books that underwent fire-fighting are to a much greater extent susceptible not only to chemical, but also to biological deterioration. Additional ingredients penetrating them contribute to the development of micro-organisms.

It is also obvious that the books have adsorbed various gaseous and aerosol products generated by combustion of various materials. Their interaction and destructive activity in the process of long-term storage require careful study, meticulous analysis and unhurried conclusions.

FURTHER RESEARCH

At the present time the first part of the work that raises no doubts, that is putting the books into phased boxes, is being consistently and thoroughly implemented. This program has been accepted at the BAN as the sole real program of collection preservation in the present complicated conditions. Taking into account that such "phased conservation" is not interminable and that development of new technologies in underway, their completion and careful testing will be followed by the stage providing for the improvement of the properties of books themselves. The goal of this subsequent stage of conservation is to bring the books to a state of conformance with the standards of permanent storage.

In order to fulfill practical and research tasks, special units dealing with conservation have been formed within the BAN organizational structure. Their activities, requiring thorough scientific qualifications, have been raised to a higher level. A number of research groups that work using modern scientific methods and theoretical prerequisites has been set up. In particular, a special preventive conservation unit has been created within the structure of the BAN's conservation department. These units develop the new and yet unknown directions of activities in the field of conservation.

In prospect, at a certain stage of development the research units at the BAN will join the Research Centre for Preservation of Cultural Heritage which is being organized in St. Petersburg under the auspices of the Getty Conservation Institute, the Russian Academy of Sciences and the City Administration. In the future it will be necessary to fill in the missing links, while forming and improving its

structure. It is quite probable that these works will be extended to the other cultural institutions of St. Petersburg. The universal nature of this idea will enable to extend the activities to other regions as well.

In the final analysis all new research and technologies will supplement and become a part of the concept of conservation at the BAN, which will, through the use of them, gradually improve.

CONCLUSION

In conclusion it is necessary to highlight the peculiarity which the BAN has attained in its work on collection preservation, by having adopted the non-conventional concept of preventive conservation.

As an ideology (philosophy) such preservation seeks to ensure the long-term storage of a collection. It is used for the purposes of planning and organization of consecutive (stage-by-stage) treatment of the imprints. Thus the departure from the usual routine practice of full individual conservation of each item is justified.

The concept infers the most complete definition of the degree and kind of damage and endeavours to ensure the prediction of the rate of processes of further disintegration of an inner book and various binding materials.

Using the concept enables to make a timely and systematic response to the activation of the destructive factors. If the possibilities of launching large-scale activities are limited, than they can be performed in the logical order within the framework of stage-by-stage treatments.

The application of stage-by-stage treatment also known as the phased conservation contributes to the system of priority assessments, which ensure the guarantee of survival of the collections for the longest possible period.

The concept ensures favourable prerequisites of the long-term planning, which would take into account the present and future technologies of collection preservation. It is quite possible that their development will make an alternative to the processes of treatment universally accepted today by many specialists and cultural institutions.

SUMMARIES

Preservation of collections at the Russian Academy of Science Library

The Library of the Academy of Sciences, founded by Peter the Great in 1714 is the biggest academic library in the world. On February 14–15, 1988 it was struck by a fire, the biggest in this century. Thanks to the efforts of the St.Petersburg BANch of the Russian Academy of Sciences,

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CORRECTION

In no. 3 of this volume unfortunately there is a mistake: The papyri documents found in the caves of the Judean desert and treated for conservation by Michael Maggen are not from the 4th, but from the 1st century BCE.

the City Administration, and numerous international organizations the situation has been quickly put under control. The Library's personnel, and conservators in particular, were facing a new period of activities, full of complexity and responsibility. These activities were developed in three directions:

- Improvement of the technologies of book drying and repository dehydration, and their rapid practical application. Development of method and implementation of disinfection of 8.1 mill. of books in the repositories.
- Development and implementation of the program of preventive conservation by means of putting a large number of damaged books into microclimatic boxes.
- Intensifying scientific research in the field of creation of new methods of rehabilitation and storage of the damaged books in the post-fire conditions.

Préservation des collections de la Bibliothèque de l'Académie des Sciences de Russie

La Bibliothèque de l'Académie des Sciences, fondée par Pierre le Grand en 1714 est la plus grande bibliothèque universitaire du monde. Les 14 et 15 février 1988 elle fut touchée par un incendie énorme , le plus gigantesque de ce siècle. On a pu rapidement maîtriser la situation grâce aux efforts conjugués de l'annexe de l'Académie des Sciences de Russie de Saint Petersbourg, de l'administration municipale ainsi que de nombreuses organisations internationales. Le personnel de la Bibliothèque et en particulier les conservateurs/restaurateurs ont dû affronter une multitude d'activités nouvelles complexes faisant appel à leur sens des responsabilités. Ces activités devaient se développer dans trois directions:

- Amélioration des méthodes de séchage des livres et de déshumidification des entrepôts d'emmagasinage ainsi que leur application immédiate. Développement d'une méthode de désinfection et application pratique de celle-ci à 8,1 mio. de livres dans les entrepôts.
- Elaboration et application d'un programme de conservation préventive en plaçant un grand nombre de livres endommagés dans des caisses microclimatiques.
- Intensification de la recherche scientifique pour développer la création de nouvelles méthodes relatives à la restauration et au stockage des livres endommagés dans des conditions correctes après leur exposition au feu.

Die Konservierung der Sammlungen in der Bibliothek der Russischen Akademie der Wissenschaften

Die Bibliothek der Russischen Akademie der Wissenschaften, gegründet von Peter dem Großen im Jahre 1714, ist eine der größten wissenschaftlichen Bibliotheken der Welt. Am 14. und 15. Februar 1988 erlebte sie eine Brandkatastrophe: die größte, die eine Bibliothek in diesem Jahrhundert getroffen hat. Dank der Anstrengungen des St.Petersburger Zweiges der Russischen Akademie der Wissenschaften, der Stadtverwaltung und zahlreicher internationaler Organisationen konnte die Lage rasch unter Kontrolle gebracht werden. Das Bibliothekspersonal und besonders die Konservatoren/Restauratoren sahen sich mit einer Fülle neuer, komplexer und verantwortungsvoller Aufgaben konfrontiert. Sie galten den folgen drei Bereichen:

- Verbesserung der Methoden zur Trocknung von Büchern und zur Entfeuchtung von Magazinräumen sowie deren unverzügliche praktische Anwendung. Entwicklung und Umsetzung einer Methode zur Desinfektion vom 8,1 Mill. Büchern in den Magazinen.
- Entwicklung und Umsetzung eines Programms zur vorbeugenden Konservierung durch Einlegen zahlreicher beschädigter Bücher in abgeschlossene Kästen mit Mikroklima.
- Intensivierung der Forschung zur Entwicklung neuer Methoden zur Wiederherstellung und zur Lagerung von beschädigten Büchern unter den Bedingungen, die sich nach einer Brandkatastrophe einstellen.

REFERENCES

1. *History of the library of the Academy of Sciences of the USSR. 1714-1964.* Moscow-Leningrad: Nauka. Acad. Sci. USSR. Libr. Acad. Sci. 1964. (in Russian).
2. The „Baer Collection" in the library of the Academy of Sciences. St. Petersburg 1992.
3. Leonov V.P.: *Recovering from the fire: Results, problems, prospects.* The Problems of Preservation of Libraries' Collections. Collection of articles. Leningrad: The Library of the Academy of Sciences of the USSR 1989: 6–14. (In Russian)
4: Hoover Sung, Carolyn, Valerii Pavlovich Leonov & Peter Waters: *Fire Recovery at the Library of the Academy of Sciences of the USSR*. American Archivist 53 (1990): 288-312.
5. Shchekatikhin ,E.A.: *Organization of disinfection of large book repositories, that have been subjected to damage during fire-fighting at the Library of the Academy of Sciences of the USSR.* The Problems ... (cf. Ref. 3): 57–76 (in Russian)
6. Nyuksha, Yu. P., O.A. Gromov, Yu.V. Pokrovskaia & Yu. V. Popov: *On the estimate of disinfection of documents and repositories at the Library of the Academy of Sciences of the USSR, subjected to damage during the fire.* The Problems ... (cf. Ref. 3): 77–85. (In Russian)
7. Waters, P.: *Phased preservation. A philosophical concept and practical approach to preservation.* Special Libraries 81 (1990): 35–43.
8. Beliaeva, I.M., & E.V. Starova: *Ensuring the preservation of library collections using microclimatic boxes.* Collection of Reports of the Participants of the Third Annual Seminar on the Problems of Preventive Conservation and Storage of Cultural Properties: Storage of the Artifacts in Small Hermetic Volumes . St. Petersburg: The State Russian Museum and the "Climate" Co. 1994: 56–58 (in Russian).
9. *Ecological problems of St. Petersburg and the ways of their solving: the scientists' view.* St. Petersburg: The Russian Academy of Sciences. The St. Petersburg Scientific Center 1993 (in Russian).

Dr. Valerii Pavolovich Leonov, Director
Dr. Yulia Petrovna Nyuksha, Senior Research Scientist, Conservation Department
The Russian Academy of Sciences Library,
199034 Birzhevaia Liniia 1
St. Petersburg
Russia

Editorial Notice

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Italics are used for emphasis, especially for distinguishing titles of books and papers.

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2. Hon. D. N.-S.: *Yellowing of modern papers.* In: Williams, J. C., ed. Preservation of paper and textiles of historic and artistic value II. Advances in Chemistry Series, 193. Washington, DC: American Chemical Society, 1981: 119–42.

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