

STABILIZATION OF CELLULOSE FIBRES WITH SODIUM BOROHYDRIDE

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Abstract. This paper reviews briefly the stabilizing of cellulose fibres with sodium borohydride and sodium borohydride combined with sodium tiosulphate and chelating agent EDTA. A rag paper (1832) was chosen for bleaching and colour reversion experiments. Accelerated aging of paper was carried out during 28 days in the dark at 75°C and 40% of RH. Brightness and the content of CHO and COOH were measured. Good stabilization results were obtained when sodium tiosulphate and EDTA were used in combination with sodium borohydride.

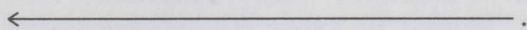
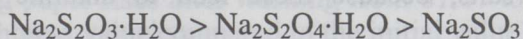
Key words: cellulose fibres, stabilization, sodium borohydride.

INTRODUCTION

From the conservation point of view, chemical bleaching may be defined as a treatment capable of decolourizing unwanted coloured materials on or in an artifact. It involves chemically changing the stains from a coloured to a colourless state. The bleaching process should also include the solubilization and removal of the staining material. For bleaching operations in paper conservation, oxidizing and reducing bleaches are used. The bleaching agents used not only react with the stain, but also with paper support. Treating paper by oxidizing agents always includes the danger of cellulose oxidation and can be considered as destructive, especially if not applied properly. It is a reason why reducing agents are widely used in the paper conservation today. Reducing agents increase the resistance of the fibres to acid hydrolysis, oxidation, alkaline degradation, and the effects of short ultraviolet wavelengths [1–3].

Reducing agents used in the paper bleaching may be divided into two categories: sulphur containing compounds and tetrahydridoborates. Sodium

tiosulphate, sodium dithionite, and sodium sulphite are the most widely used sulphur containing compounds. The sulphur containing reducing agents are used dissolved in water and are stable enough in this form. The relative reducing power of these reagents is as follows [4]:

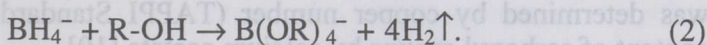
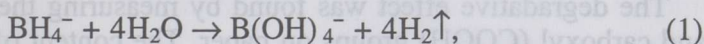


redox potential, bleaching effect

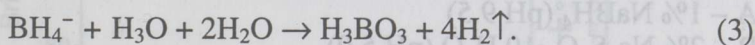
Sulphured reducing compounds are used as antichlors after treatment with chlorine bleaches and for stabilizing hydrogen boroxide. They can also reduce and hence decolourize organoferric complexes ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$), but the reaction is reversible and the bleaching effect is thus paralyzed [3].

Three derivatives of borohydrides have been researched with conservation applications in mind. These are sodium, tetramethylammonium, and tetraethylammonium salts. Their reducing action is fairly similar, but the working properties are quite different [3]. In comparison with the sulphur compounds the reducing power of tetrahydridoborates is far more extensive [5]. In addition to the species mentioned above, they react with acyl chlorides, esters, aldehydes, and ketones. They reduce carbonyl groups responsible for yellowing to primary alcohol groups. Regeneration of oxidized terminal groups is limited and very slow [2, 6, 7]. In addition to their greater scope of reaction, borohydrides have the advantage of being soluble in many organic solvents besides aqueous media.

Tetrahydridoborates (BH_4^-) decompose in water or alcohol to yield various boron products and hydrogen gas:



Evolution of hydrogen gas can lead to physical damage of the paper artifact [1-3, 6-9]. It is, therefore, very important to keep any decomposition of borohydride to a minimum. Borohydride solutions should not be used immediately after being made up but be allowed to equilibrate (by self-buffering) until the hydrogen evolution has slowed down (Eq. (3)).



An aqueous solution of sodium borohydride is alkaline, its pH is about 9.5. At this pH level the decomposition reaction is relatively slow and the most effective bleaching reaction occurs. Hydrogen gas formation may also be slowed down by using alcohol solvents but then the bleaching efficiency is lower than in case of aqueous solutions of sodium borohydride.

The decomposition reaction of tetrahydridoborates is increased also by metal ions (Fe^{3+} , Cu^{2+} , Mn^{2+} , Ca^{2+} , Ba^{2+} , Mg^{2+}) [6]. Therefore, it is

essential that only deionized or distilled water be used. The addition of chelation agents (e.g. 0.1 M EDTA) to aid in solubilizing and removing the metal ions can be helpful [3].

After treatment the paper must be well washed in order to remove all soluble sodium salts, because these lead to alkaline degradation of cellulose [2].

EXPERIMENTAL METHODS

A rag paper (moisture content 3.62%, ash content 1.16%, content of extractives 0.91%, published in Moscow, Russia, in 1832) was used for bleaching and colour reversion experiments. The procedures were carried out at room temperature (22 °C) with less than 3 °C variation among the various treatments. Distilled water was used in the preparation of all the solutions. The pH values were checked and adjusted to 5.0 and 9.5 with acetic acid or sodium hydroxide. Paper samples were bleached with each solution for four different times (2, 6, 14, and 26 min). After bleaching the samples were transferred to three different washing trays (with 1.5 l of distilled water) and washed 10 min to remove residual chemicals. The paper was dried between acid-free blotters and after approximately 18 h the reflectance was measured.

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

The degradative effect was found by measuring the aldehyde (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].

Accelerated aging of paper was carried out during 28 days in the dark at 75 °C and 40% of RH. After accelerated aging brightness and the content of CHO and COOH were measured.

Bleach solutions

Seven different bleach solutions were used:

A – 1% NaBH₄ (pH 9.5)

B – 2% Na₂S₂O₃·10 H₂O (pH 5.0)

C – 2% Na₂S₂O₃·10 H₂O (pH 9.5)

D – 2% Na₂S₂O₃·10 H₂O / 0.1 M EDTA (pH 5.0)

E – 2% Na₂S₂O₃·10 H₂O / 0.1 M EDTA (pH 9.5)

F – solutions D (pH 5.0) + E (pH 9.5)

G – solution F / 1% NaBH₄ (pH 9.5)

Borohydride solutions were not used immediately but allowed to equilibrate (by self-buffering) for 30 min, until hydrogen evolution had slowed down.

RESULTS

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

Brightness values after bleaching

The bleach solutions may be ranked in the following order of increasing brightness (Table 1, Fig. 1).

Table 1

Results of the measurements of brightness after 14 min bleaching

Bleach solution	Brightness value after bleaching, %	Increase in brightness value after 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

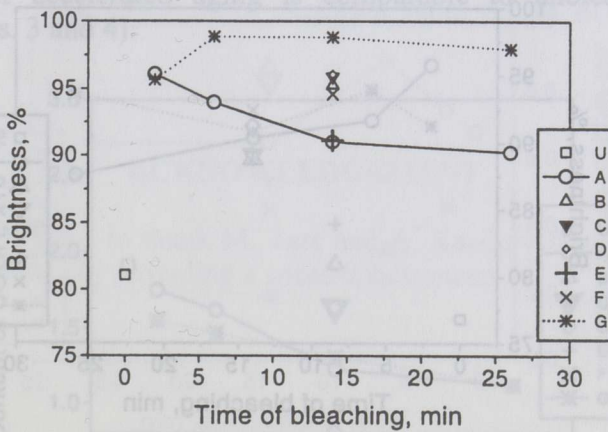


Fig. 1. Brightness of paper after bleaching. U, unbleached; A-G, bleached using different bleach solutions.

Colour reversion of bleached samples

The rate of colour reversion can often be correlated to the total brightness change (Table 2, Figs. 1 and 2).

The paper samples treated with sodium borohydride solutions have a higher bleaching stability than those treated with sodium tiosulphate solutions. The washing procedure is very important, because some chromophores are soluble in water. Washed unbleached paper shows a good brightness level after aging compared to the unbleached sample. All paper samples have a higher brightness level after accelerated aging than the unbleached sample (Table 3, Figs. 1 and 2).

Table 2

Results of measurements of brightness after accelerated aging (28 days)

Bleach solution	Brightness value after 14 min bleaching, %	Decrease of brightness value after accelerated aging, %
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
G	98.81	8.07

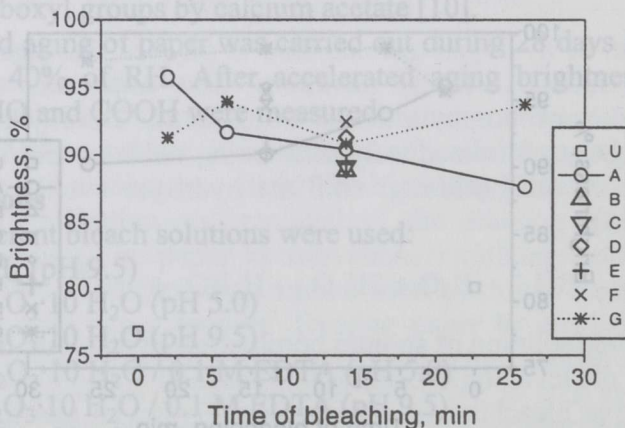


Fig. 2. Brightness of bleached paper after accelerated aging (28 days). U, unbleached; A-G, bleached using different bleach solutions.

Brightness and the content of COOH and CHO groups

Bleaching		Brightness, %		Content of COOH groups, $\times 10^{-3}$ %		Content of CHO groups, copper number	
solution	time, min	after bleaching	after aging (28 days)	after bleaching	after aging (28 days)	after bleaching	after aging (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

Changes in the content of carboxyl and aldehyde groups

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

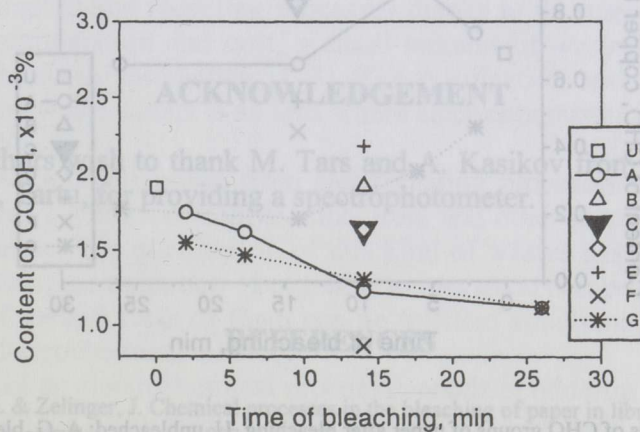


Fig. 3. Changes of COOH groups of paper after bleaching. U, unbleached; A–G, bleached using different bleach solutions.

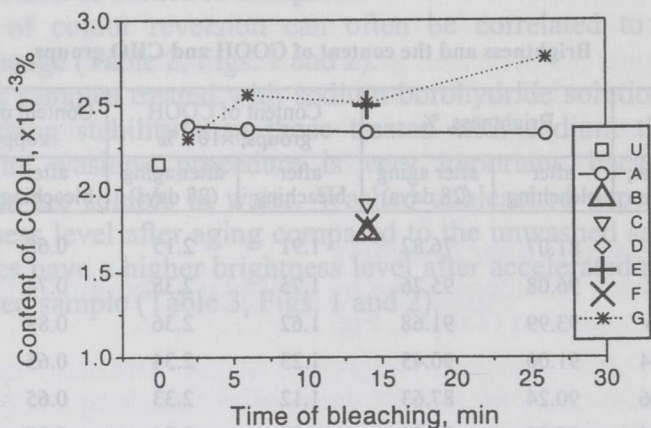


Fig. 4. Changes of COOH groups of bleached paper after accelerated aging (28 days). U, unbleached; A–G, bleached using different bleach solutions.

The biggest decreasing of CHO groups is obtained by using bleach solution G (Fig. 5). It seems that a correlation exists between the content of CHO groups (which are responsible for yellowing) and the brightness value (Tables 1–3). Copper number values of bleached papers did not show any remarkable increasing tendency during accelerated aging, on the contrary, papers treated with bleach solutions A, F, and G had a smaller content of CHO groups than unbleached paper (Table 3, Figs. 5 and 6).

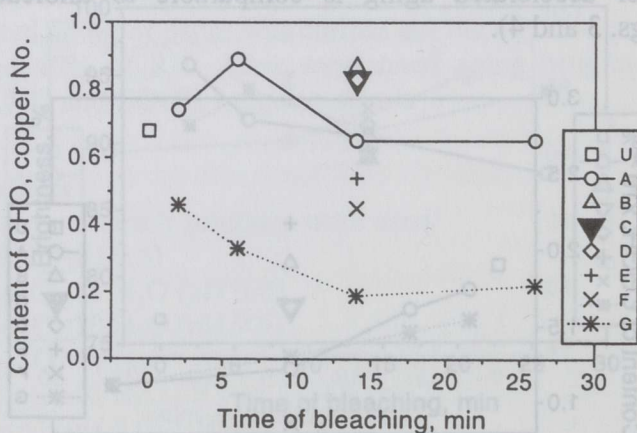


Fig. 5. Changes of CHO groups of paper after bleaching. U, unbleached; A–G, bleached using different bleach solutions.

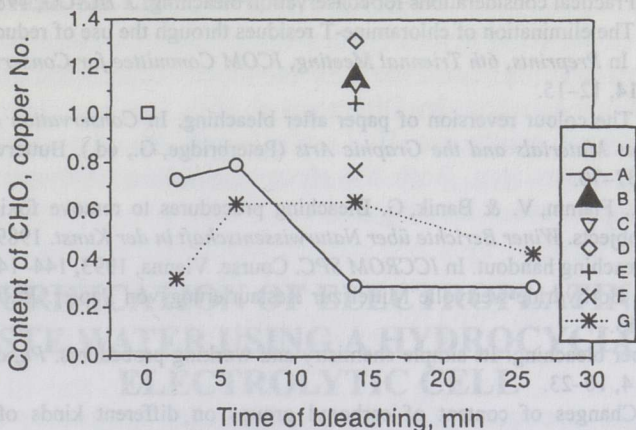


Fig. 6. Changes of CHO groups of bleached paper after accelerated aging (28 days). U, unbleached; A-G, bleached using different bleach solutions.

CONCLUSIONS

The destruction or removal of the chromophore systems is difficult, because most chemical bleaching methods used in the conservation of paper always cause some damage.

In comparison with oxidants, reducing bleaches (especially borohydrides) cause no degradation of cellulose. On the contrary, they have an ability to improve the permanence of cellulose fibres.

Sulphur reducing agents alone have a quite poor colour stabilization and reducing power, but the use of sodium tiosulphate combined with sodium borohydride (addition of chelation agent 0.1 M EDTA) gives a good result.

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TSELLULOOSI KIUDUDE STABILISEERIMINE NAATRIUMBOORHÜDRIIDIGA

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On uuritud naatriumboorhüdriidi stabiliseerivat toimet tselluloosi kiududele koosmõjus naatriumtiosulfaadi ja EDTA-ga. Uuringutes kasutati 1832. aastal Venemaal toodetud kaltsupaberit. Paberit vanandati termiliselt 28 päeva pimedas temperatuuril 75 °C ning 40% relatiivse niiskuse juures. Valgedus, CHO ja COOH rühmade sisaldus määrati enne ja pärast termilist vanandamist.

