

ASSESSING THE RISKS OF ALKALINE DAMAGE DURING DEACIDIFICATION TREATMENTS OF OXIDIZED PAPER

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ABSTRACT—The sensitivity of oxidized cellulose to damaging beta-elimination reactions was studied to define safe pH conditions and treatment times beyond which damage from alkaline treatment may occur; whether damage caused by alkaline treatment was affected by the type or amount of oxidation was also investigated. Cotton paper was oxidized using UV-A radiation, a hydrogen peroxide solution, or a sodium metaperiodate solution. Following oxidation, samples were soaked at room temperature in carbon-dioxide-free calcium hydroxide baths, at pH 8.5, 10.0, or 12.5, for 20 or 60 minutes. Changes to the molecular weight of the cellulose as a function of the amount of oxidation, treatment bath pH, and treatment time, were monitored to understand which conditions cause degradation to occur. The UV-A and hydrogen peroxide oxidized samples, simulating naturally oxidized papers, showed minimal sensitivity to beta-elimination reactions in baths up to pH 10.0; slight degradation was observed during treatment at pH 12.5. By contrast, sodium metaperiodate oxidized samples, which did not mimic naturally oxidized papers, were markedly degraded in pH 10.0 and 12.5 baths, with more degradation occurring at higher pH. For the oxidized papers found to be sensitive to beta-elimination reactions, longer treatment times led to more degradation.

TITRE—L'évaluation des risques de dommages dus à l'alcalinité lors des traitements de désacidification du papier oxydé. **RÉSUMÉ**—La sensibilité de la cellulose oxydée aux réactions préjudiciables de bêta-élimination a été étudiée afin de définir les niveaux de pH et les temps de traitement au delà desquels des dommages causés par le traitement alcalin peuvent se produire. On a également étudié si ces dommages étaient affectés par le type ou le degré d'oxydation. Des échantillons de papier coton ont été oxydés soit par les rayons ultraviolets A, soit par une solution de peroxyde d'hydrogène, ou encore par une solution de métaperiodate de sodium. Après oxydation, les échantillons ont été plongés pendant 20 ou 60 minutes dans des bains à température ambiante d'hydroxyde de calcium ne contenant pas de dioxyde de carbone et dont le pH était égal à 8,5, 10, ou 12,5. Les change-

ments dans le poids moléculaire de la cellulose en fonction de la quantité d'oxydation, le pH du bain de traitement et le temps de traitement ont été considérés afin d'identifier les conditions qui favorisent la dégradation. Les échantillons oxydés par les rayons ultraviolets A et le peroxyde d'hydrogène, simulant les papiers naturellement oxydés, ont montré une sensibilité minimale aux réactions de bêta-élimination dans les bains jusqu'à un pH aussi élevé que 10 ; on a observé une légère dégradation pendant le traitement à un pH de 12,5. Par contre, les échantillons oxydés par le métaperiodate de sodium, qui ne simulaient pas les papiers naturellement oxydés, ont été nettement dégradés dans les bains à un pH de 10 ou 12,5 avec plus de dégradation se produisant à un pH plus élevé. Pour les papiers oxydés sensibles aux réactions de bêta-élimination, de plus longs temps de traitement ont causé plus de dégradation.

TITULO—Evaluación de riesgos de los daños producidos por la alcalinización en el tratamiento de papeles oxidados. **RESUMEN**—Se estudió la sensibilidad de la celulosa oxidada hacia las reacciones dañinas de beta-eliminación para definir las condiciones seguras de pH y tiempo de duración del tratamiento más allá de las cuales pudieran ocurrir daños por el tratamiento de alcalinización; igualmente se investigó si el daño causado por el tratamiento de alcalinización es afectado por el tipo o cantidad de oxidación presente. Se oxidaron papeles de algodón usando radiaciones UV-A, una solución de peróxido de hidrógeno, o una solución de metaperiodato de sodio. Posterior a la oxidación, las muestras fueron impregnadas, a temperatura ambiente, en baños de hidróxido de calcio libres de dióxido de carbono, con pH 8.5, 10.0, ó 12.5, durante 20 ó 60 minutos. Los cambios del peso molecular de la celulosa fueron monitoreados para entender cuales condiciones llevaron a la degradación en función a la cantidad de oxidación presente, el pH del baño del tratamiento, y el tiempo del tratamiento. Las muestras oxidadas con UV-A y con peróxido de hidrógeno, que simulaban papeles oxidados de manera natural, mostraron una sensibilidad mínima a las reacciones de beta-eliminación en baños de hasta un pH 10.0; una pequeña degradación se observó

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durante el tratamiento a un pH 12.5. Por contraste, las muestras oxidadas con metaperiodato de sodio, que no simulaban papeles oxidados de manera natural, fueron marcadamente degradadas en baños con pH 10.0 y 12.5, ocurriendo mayor degradación a pH superiores. En el caso de los papeles oxidados que se determinaron ser sensibles a las reacciones de beta-eliminación, los tratamientos que tomaron más tiempo llevaron a mayores degradaciones.

TÍTULO—Avaliação dos riscos dos danos produzidos pela alcalinização durante a desacidificação em tratamento de papéis oxidados. RESUMO—Estudou-se a sensibilidade da celulose oxidada nas reações danificadas de beta-eliminação a fim de se definirem as condições seguras de pH e tempos de duração do tratamento depois dos quais poderiam ocorrer danos causados pela alcalinização; investigou-se também se o dano causado pelo tratamento de alcalinização foi afetado pelo tipo ou quantidade de oxidação presente. Papéis de algodão foram oxidados usando-se radiação UV-A, solução de peróxido de hidrogênio ou solução de metaperiodato de sódio. Após a oxidação, amostras foram impregnadas em temperatura ambiente em banhos de hidróxido de cálcio livres de dióxido de carbono, com pH=8,5, 10 ou 12,5 durante 20 ou 60 minutos. As mudanças do peso molecular da celulose foram monitoradas para se entender quais foram as condições que levaram à degradação em função da quantidade de oxidação presente, o pH do banho do tratamento e o tempo do tratamento. As amostras oxidadas com UV-A e com peróxido de hidrogênio, as quais simulavam papéis oxidados naturalmente, mostraram uma sensibilidade mínima às reações de beta-eliminación em banhos com um pH de até 10; observou-se uma pequena degradação durante o tratamento com um pH de 12,5. Em contrapartida, as amostras oxidadas com metaperiodato de sódio, que não simulavam papéis oxidados naturalmente, sofreram degradação acentuada em banhos com pH=10 e 12,5, havendo maior degradação com pH mais altos. No caso dos papéis oxidados considerados sensíveis às reações de beta-eliminación, os tratamentos mais longos acarretaram maiores degradações.

1. INTRODUCTION

Conservation treatments of oxidized paper with aqueous alkaline baths pose a challenge: while intended to stabilize paper by removing and neutralizing the

acidity in the fibers, there is a concern that alkaline baths may instead cause damage to the oxidized cellulose molecules in the paper (Couch 1986; Gerbracht and Brückle 1997). Such damage would decrease the molecular weight of the cellulose, permanently weakening the paper. When the molecular weight is severely compromised, paper cannot absorb energy introduced by bending or flexing, and therefore would be liable to break if handled. If this were the result, the beneficial outcome of an alkaline treatment would be negated. Though direct observation of molecular damage from alkaline treatment baths has not been reported, proposed treatments have been designed to avoid the conditions under which alkaline attack occurs. Specifically, temperatures are to be kept moderate (Santucci and Zappala 2001), pH is usually held below 9 (Kolar 1997; Giorgi et al. 2002) or 10 (Gerbracht and Brückle 1997), and treatment times are kept modest (Hey 1979; Couch 1986).

As these suggestions indicate, the perception that alkaline baths pose the risk of damaging oxidized cellulose remains widespread. The expectation that alkali baths will have a deleterious effect on paper is perhaps derived from reports coming out of the pulp and paper science community, where it is indeed an issue (Davidson 1940; Richards 1971; Varma and Chavan 1995). However, the temperatures, treatment times, and pH conditions of the alkaline processes used by the paper industry often exceed those used in conservation (Machell and Richards 1958; O'Meara and Richards 1958; Richards 1971). In addition, the way in which paper is oxidized for those studies—using sodium metaperiodate (NaIO_4)—is unique and creates an oxidized cellulose that is not made during natural aging.

The present study was designed to define safe pH conditions and treatment times beyond which the risk of damage during treatment may be significant, and to investigate whether any damage incurred by alkaline treatment is affected by the type or amount of oxidation.

2. BACKGROUND

2.1 THE NATURE OF OXIDIZED CELLULOSE

In designing a controlled experiment to assess the risk of alkaline damage to oxidized papers, the first challenge was the preparation of oxidized samples

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that represented naturally aged, oxidized papers. There are many ways that papers experience oxidative deterioration: exposure to light; reaction with atmospheric oxygen, particularly in the presence of iron or copper catalysts; or as the result of bleaching treatments during manufacture or conservation. Cellulose (Fig. 1a) oxidation results in the formation of carbonyl and carboxyl groups that are incorporated into the cellulose molecule as aldehydes, ketones, and carboxylic acids, replacing some of the hydroxyl groups. A precise determination of where oxidized functional groups are located—at which position on a single glucopyranose ring or along the cellulose molecular chain—has been impossible so far.

To date, the most specific description of naturally oxidized cellulose has come from a study of the products of various oxidation conditions, including light, hydrogen peroxide, and chlorine bleaches (Whitmore and Bogaard 1994). The reaction products and changes to the cellulose molecular weight indicated that all three oxidants react randomly, with reaction occurring at any of the three hydroxyl-containing carbon atoms (C_2 , C_3 , C_6), or the two 1,4-glucosidic linkages (C_1 , C_4) that connect glucose rings, at any ring along an amorphous cellulose chain segment.

Reactions at the C_1 and C_4 on the glucopyranose ring lead to cellulose chain breakage and the formation of aldehydes or carboxyls at the new chain ends (fig. 1b). Reactions at the C_2 , C_3 , or C_6 carbons lead to the formation of oxidized groups (aldehydes and ketones) on the ring (fig. 1c). This second set of reactions probably occurs without chain breaks, but the oxidized groups formed create weak links within the cellulose chain. The location of these weak sites along the interior of the chain is indicated by an increased rate of hydrolysis in thermal aging of oxidized papers (Whitmore and Bogaard 1995). Since light exposure and chemical bleaching produce roughly the same types and distributions of oxidized groups, it suggests that the same products would result from oxidation during natural aging (Whitmore and Bogaard 1994). In the current study, to mimic the natural oxidation most likely to be encountered in a conservation environment, papers were oxidized using near-ultraviolet radiation or solutions of hydrogen peroxide.

In addition to these samples, papers were also oxidized using sodium metaperiodate, an oxidant that reacts primarily at the C_2 and C_3 positions (Potthast et al. 2006). The oxidation results in the formation of aldehyde groups at the two hydroxyl positions and the opening of the glucopyranose ring (fig. 1d). The

product of cellulose oxidized in this manner is sometimes referred to as dialdehyde cellulose (DAC). While it is unlikely that this oxidation mechanism occurs in nature (Meller 1960; Potthast et al. 2006), this type of cellulose oxidation was included in the study because the resulting molecule is known to be sensitive to alkaline degradation (Meller 1951; O'Meara and Richards 1958; Richards 1971).

2.2 ALKALINE DAMAGE TO OXIDIZED CELLULOSE

When oxidized groups are located along an intact cellulose chain, primarily on the amorphous tie chains that bridge the crystalline regions and impart strength to the fiber (Rowland and Cousins 1966), the risk of incurring damage during alkaline treatment is present. Under alkaline conditions, reactions known as beta-elimination (β -elimination) reactions may take place at the oxidized sites (fig. 2). During these reactions, a hydrogen ion (H^+) is abstracted from a carbon located next to the oxidized group (at the α -position) by a hydroxyl ion (OH^-) in solution. Next, the bonds of the ionized cellulose rearrange, ultimately breaking the bond located two positions away from the oxidized group (at the β -position). Since the action of random oxidants—such as light or hydrogen peroxide—creates oxidized functional groups at many locations within the cellulose molecule, many β -elimination reactions are possible. Some of these reactions will break the link in the cellulose chain, decreasing molecular weight and fiber strength. In this study, the potential for alkaline damage through these cellulose reactions is assessed by measuring changes in molecular weight after alkaline treatment.

3. EXPERIMENTAL APPROACH

3.1 MATERIALS

Sheets of Whatman Grade no. 1 Qualitative Filter Paper (W1) were used as received from Whatman for all experiments. This cotton filter paper was chosen because it is very pure and allows for sensitive analysis of the molecular weight and carbonyl content. Made of 98% alpha cellulose, it is an ideal material for studying cellulose degradation.

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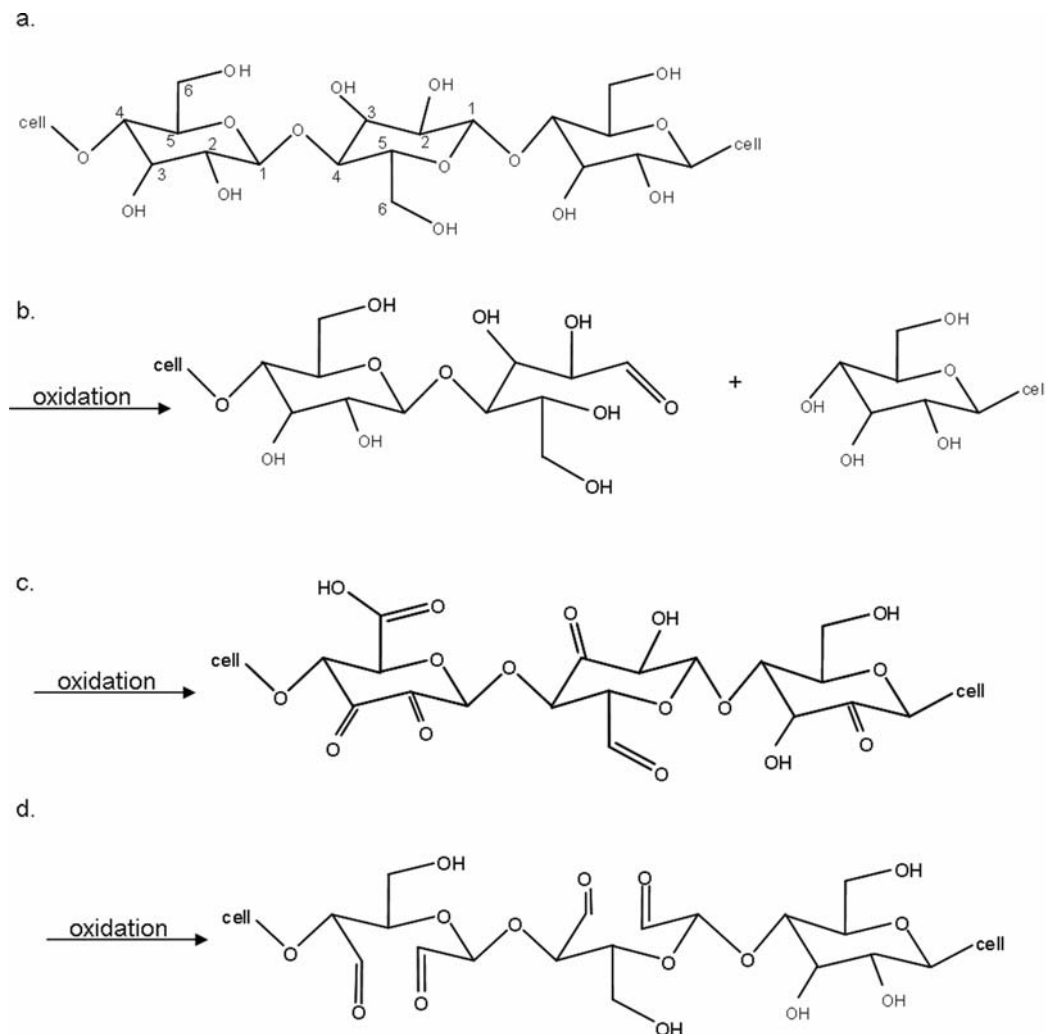


Fig. 1. Different modes of oxidation for cellulose: (a) unoxidized cellulose; (b) cellulose undergoing oxidation at a C₁ carbon, resulting in chain scission and aldehyde formation; (c) ketone, aldehyde, or carboxyl formation from oxidation at C₂, C₃ or C₆; (d) dialdehyde cellulose formation at C₂ and C₃ carbons from oxidation with sodium metaperiodate (NaIO₄)

3.2 OXIDATION

3.2.1 UV-A Radiation

One sheet of W1 paper, 46 × 56 cm, was oxidized under a bank of Q-Panel A-351 UV-A lamps (emitted wavelengths: 320–400 nm). The average irradiance of the light bank was measured to be 43.3 W/m² at the sample position. Exposures were carried out at 25°C

and 50% relative humidity in a constant environment room.

The sheet was laid on a metal mesh screen, placing the sheet 14 mm below the light bank. At 2520 hours of UV-A exposure, half of the sheet was removed and the original sheet was placed back under the light bank for continued oxidation. At 6720 hours, the second half of the sheet was removed from the light bank.

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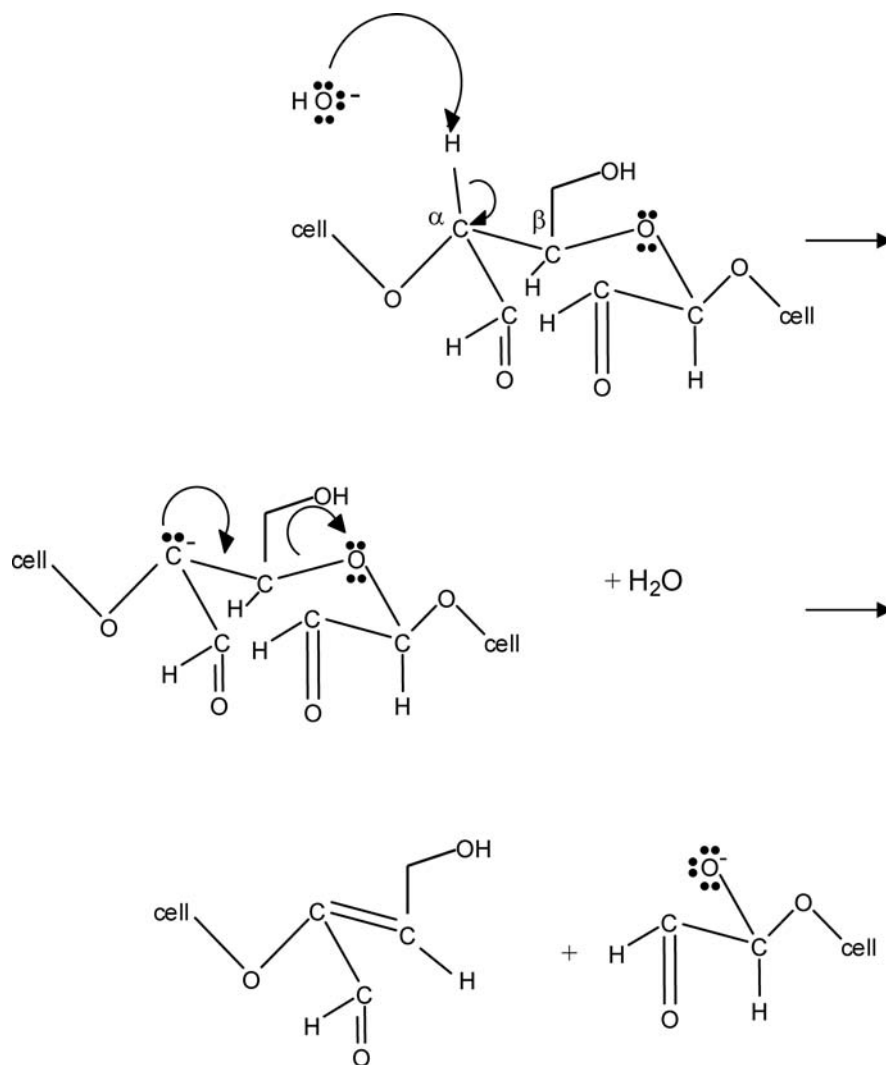


Fig. 2. Mechanism of beta-elimination reaction when sodium metaperiodate oxidized cellulose is placed in an alkaline environment

3.2.2 H_2O_2 Solution

Trimmed W1 sheets, 13 cm \times 15 cm, were oxidized at ambient laboratory conditions in a covered glass Pyrex dish with 600 mL 10% hydrogen peroxide (H_2O_2) solution for 1, 24, or 96 hours. The 10% H_2O_2 solution was made by diluting unstabilized, puriss (98.5% pure) grade 30% hydrogen peroxide with distilled water. After soaking, damp sheets were

placed between blotting paper, weighted under glass, and allowed to dry.

3.2.3 NaIO_4 Solution

Trimmed W1 sheets, 13 cm \times 15 cm, were soaked at ambient conditions in a prepared 0.1M solution of NaIO_4 for 0.5, 1, or 2 hours, respectively. After oxidation, samples were washed under cold running

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tap water for 30 minutes. Rinsed samples were dried between blotting paper and weighted under glass.

Initially, samples were placed between blotting paper and dried in a manner similar to the H_2O_2 oxidized samples. However, it was observed empirically that when excess NaIO_4 was not rinsed out, over time the oxidized paper turned a deep yellow color, white crystals erupted from the fiber network, and the paper became extremely brittle. Inadequately rinsed samples were therefore removed from the study and the rinsing step was added to the oxidation procedure.

3.3 ALKALINE TREATMENT BATHS

Following oxidation, the unoxidized W1 and the three sets of oxidized papers were cut into six pieces so that they could be soaked in the three alkaline treatment baths. Two different treatment times were selected for this study, 20 or 60 minutes. Calcium hydroxide [$\text{Ca}(\text{OH})_2$] was chosen as the alkaline salt. For each treatment bath, approximately 1000 mL of water was placed in a $20 \times 29 \times 5$ cm glass baking dish. A saturated solution of $\text{Ca}(\text{OH})_2$ was added drop-wise to the water bath to obtain the target pH. The pH was monitored throughout each treatment using an Orion ROSS pH microprobe electrode attached to a Thermo-Orion model 720A benchtop pH meter. A separate treatment bath was used for each oxidation method to prevent any cross-contamination of the samples. After each treatment bath, samples were placed between blotter papers, weighted under glass, and allowed to dry. Samples were not rinsed after alkaline treatments.

Three treatment bath pHs were chosen for use in this study, pH 8.5, 10.0, and 12.5. These pHs were specifically chosen to span from traditionally accepted (pH 8.5) to typically avoided (pH 12.5). Since it was not known at the beginning of the experiment which, if any, pHs might cause β -elimination degradation, it was necessary to study a variety of alkaline pHs so that a delineation between safe and unsafe pHs might be made.

Alkaline treatment baths were initially conducted in open air laboratory conditions but it was observed that the pH 8.5 and pH 10.0 $\text{Ca}(\text{OH})_2$ baths did not maintain constant pH throughout the course of the experiment. The pH of these baths decreased over time, presumably due to the absorption of atmospheric carbon dioxide (CO_2) by the solution, which forms carbonic acid, lowering the solution pH. Fig-

ure 3 shows the change in pH of the three $\text{Ca}(\text{OH})_2$ treatment baths during open air experiments. For the pH 8.5 bath, the pH fell below 7.0 within 15 minutes. For the pH 10.0 bath, the pH dropped to about 7.0 in 40 minutes. The rapid change in pH due to reaction with CO_2 was a result of the very low ionic strength of the solutions and the large surface-to-volume ratio of the baths prepared in baking dishes. The pH 12.5 bath maintained its pH throughout the course of the experiment as it was saturated with $\text{Ca}(\text{OH})_2$.

Since the rate of pH drop is a function of the surface area of the bath and the quantity of solution used, its decrease will vary based upon the treatment bath setup. To achieve better pH stability during conservation treatment, conservators should consider quantitatively measuring the pH of their treatment baths, using solutions soon after preparation, and monitoring solution pH during treatment to make sure the desired pH is actually used. In this study, to maintain a constant pH during the course of the alkaline treatments, the treatments were performed at room temperature (RT) in a glove bag filled with dry, high-purity nitrogen gas.

Monitoring the pH, it was possible to observe that the pH was held constant by excluding CO_2 throughout the course of the alkaline treatments. In this way, it was possible to link any alkaline sensitivity to the pH used during the experiment. Had the pH been allowed to drift to lower values during the experiment, it would not have been possible to pinpoint which pH led to degradation. Removing the ambient CO_2 also meant that it was not necessary to change the treatment solution during a 60-minute treatment as the pH was constant for the duration of the experiment.

3.4 CELLULOSE ANALYSIS

3.4.1 Carbonyl Content Analysis

To properly calculate the carbonyl content of papers before and after oxidation, the dry weight of each sample was needed. To determine this value, the moisture content of each sample was measured by using the ASTM standard test method D-644. Once the moisture content was determined, measured weights were reduced by that percentage to calculate the dry weight.

The carbonyl content of samples was assayed using a modified hydrazine method (Albertsson and Samuelson 1962), despite its known limitations

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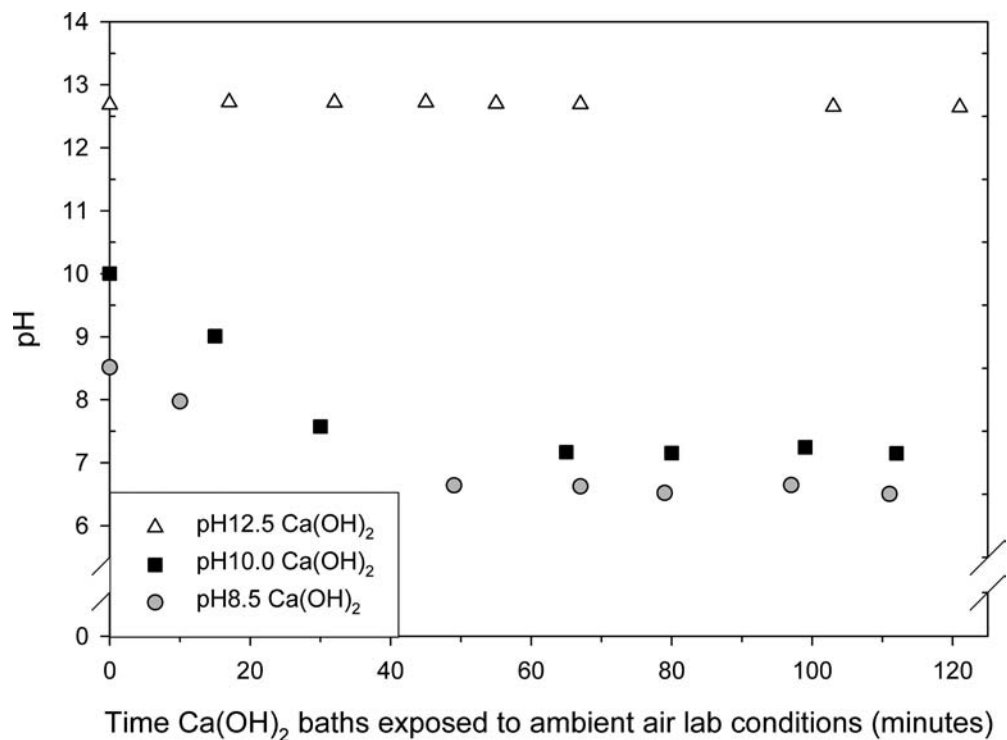


Fig. 3. Effect of atmospheric carbon dioxide (CO₂) on open air calcium hydroxide treatment baths

measuring high carbonyl contents of periodate oxidized samples (Norstedt and Samuelson 1966). Seven mL of 0.5M hydrazine solution were added to a weighed sample and left to soak for 24 hours. Each sample was then rinsed in 200 mL distilled water over 15 minutes to wash out unreacted hydrazine. In an Erlenmeyer flask, the rinsed sample was dissolved in 3.2 mL 70% sulfuric acid and stirred at 35°C for one hour. Ten mL water and 40 mL 0.13M p-dimethylaminobenzaldehyde solution were then added to the mixture. Once cooled to RT, the percent transmission of the solution was measured at 460 nm on a Gretag Macbeth Color Eye 7000 spectrophotometer. Each carbonyl content value reported is the average of results for three replicate paper samples.

3.4.2 Gel Permeation Chromatography (GPC)

A modification of the solvent exchange protocol developed by others (McCormick et al. 1985; Dupont 2003; Strlic and Kolar 2003) was used to dissolve the

W1 control, oxidized, and oxidized and alkali-treated samples for GPC analysis. A sample weighing approximately 0.04 g was immersed in 5 mL distilled water for 24 hours. Each sample was then immersed in 5 mL methanol for two, one-hour baths followed by two, one-hour baths in 5 mL dimethylacetamide (DMAc). Each sample was then dissolved in 5 mL 8% (w/v) lithium chloride in dimethylacetamide (LiCl/DMAc).

Immediately preceding GPC analysis, solutions were diluted to 0.0625% (w/v) cellulose in 0.5% (w/v) LiCl/DMAc. Molecular weight distributions (MWD) were measured by GPC using a Waters 2695 Separations Module (at 70°C) coupled to a Waters 2414 refractive index detector (at 50°C). Three Waters HR Ultrastayragel columns in series, HR5, HR4, and HR3, separated the masses. Eight pullulan standards covering the range of molecular weights were dissolved in the LiCl/DMAc solvent and analyzed to generate a calibration curve. The average of three injections for each sample solution was used to determine the weight-average molecular weight (M_w). Values reported are the average of at least two solutions and hence six injections. The degree of

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Table 1. Carbonyl content and DP before and after oxidation

| | Carbonyl content (mmol/100g) | DP |
|-----------------------------------|---------------------------------|------------|
| Unoxidized | | |
| W1 Control | 0.6 ± 0.1 | 2760 ± 110 |
| Oxidized | | |
| UV-A light | | |
| 2520 hr | 3.1 ± 0.2 | 1820 ± 150 |
| 6720 hr | 4.2 ± 0.5 | 1390 ± 30 |
| 10% H ₂ O ₂ | | |
| 1 hr | 3.8 ± 0.1 | 1230 ± 80 |
| 24 hr | 8.9 ± 0.6 | 680 ± 40 |
| 96 hr | 10.7 ± 0.1 | 580 ± 10 |
| 0.1M NaIO ₄ | | |
| 0.5 hr | 12.4 ± 0.8 | 1860 ± 50 |
| 1 hr | 23.1 ± 3.5 | 1990 ± 50 |
| 2 hr | 41.8 ± 2.2 | 1910 ± 140 |

polymerization (DP) was calculated by taking the M_w and dividing by the monomer molecular weight of cellulose, 162 g/mol.

4. RESULTS

Table 1 summarizes the carbonyl content and the DP of samples before and after oxidation. The unoxidized W1 control contained a small concentration of carbonyl groups, 0.6 millimoles of carbonyls per 100 grams of sample (mmol C=O/100g cellulose), many of which were probably aldehydes on the reducing end of the cellulose chains (Wilson and Parks 1974). Oxidation levels of W1 paper ranged from 3.1 mmol C=O/100g cellulose for the UV-A 2520 hr sample to 41.8 mmol C=O/100g cellulose for the 0.1M NaIO₄ 2hr sample.

In addition to increasing the level of oxidation, exposing samples to various oxidative environments caused a decrease in molecular weight from the original unoxidized W1 DP = 2760. This result was expected for samples oxidized using UV-A light or H₂O₂, for these oxidants have been shown to break chains as well as produce carbonyl and carboxyl groups (Whitmore and Bogaard 1994). Degradation of cellulose in NaIO₄ solution was unexpected. The NaIO₄ oxidized papers had an average DP = 1860, 1990, and 1910 for 0.5, 1, and 2 hours of oxidation, respectively. The oxidation should have been specific to the C₂ and C₃ positions of the anhydroglucose and should have merely opened the ring and not broken the chain. Nevertheless, some chain breaking degradation was

observed. Previously it was observed that cellulose will degrade in the presence of NaIO₄ if the solution is exposed to light (Head 1953; Painter 1988). The fluorescent lights in the laboratory were turned on during oxidation with NaIO₄; the unexpected degradation of the W1 papers may be the result.

Following the oxidation step, samples were treated in one of the three pH alkaline baths. Table 2 summarizes the DP of samples following alkaline treatment as a function of treatment pH and treatment time. In some instances, for example the UV-A 2520 hr sample treated at pH 8.5 for 60 minutes (UVA 2520 pH8.5 60), alkaline treatment appeared to have had no effect on DP. In others, such as the 0.1M NaIO₄ 2hr pH12.5 60, alkaline treatment caused a large decrease in the DP. In a few instances, as with the 10% H₂O₂ 1hr 20, alkaline treatment appeared to cause an increase in the DP relative to the oxidized only sample. However, when the experimental error was taken into account, the DP of these samples remained unchanged by alkaline treatment. Qualitatively, it appeared that alkaline treatments had some effect on the DP of oxidized paper. However, while changes to the DP following the alkaline treatment can be viewed as evidence of β -elimination reactions, a change to the DP alone does not accurately reflect the amount of alkaline degradation that took place; chain breaks more precisely reflect the effect of an alkaline treatment on oxidized paper. In order to assess the extent of alkaline degradation, the number of chains that were broken during treatment must be calculated. Chain break calculations are derived from DP values and are explained in the following section.

5. DISCUSSION

5.1 ALKALINE DAMAGE FROM TREATMENTS AT DIFFERENT PH

The number of β -elimination, chain-breaking reactions caused by placing oxidized paper into alkaline treatment baths was calculated using the formula:

$$\begin{aligned} \text{Chain breaks (mmol/100g cellulose)} \\ = 1235/DP_t - 1235/DP_0 \end{aligned} \quad (1)$$

where DP_t is the measured degree of polymerization following both oxidation and alkaline treatment, and DP₀ is the degree of polymerization measured following oxidation alone (Whitmore and Bogaard

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Table 2. DP following alkaline treatment

| | DP (following alkaline treatment) | | | | | |
|-----------------------------------|-----------------------------------|------------|------------|------------|------------|------------|
| | pH8.5 | | pH10 | | pH12.5 | |
| | 20 min. | 60 min. | 20 min. | 60 min. | 20 min. | 60 min. |
| Unoxidized | | | | | | |
| W1 Control | 2680 ± 170 | 2540 ± 260 | 2560 ± 160 | 2420 ± 360 | 2500 ± 120 | 2500 ± 270 |
| Oxidized | | | | | | |
| UV-A light | | | | | | |
| 2520 hr | 1820 ± 60 | 1820 ± 50 | 1800 ± 90 | 1820 ± 50 | 1590 ± 60 | 1640 ± 40 |
| 6720 hr | 1380 ± 10 | 1360 ± 20 | 1340 ± 0 | 1320 ± 20 | 1200 ± 10 | 1190 ± 10 |
| 10% H ₂ O ₂ | | | | | | |
| 1 hr | 1350 ± 50 | 1240 ± 30 | 1350 ± 40 | 1290 ± 10 | 1290 ± 10 | 1000 ± 20 |
| 24 hr | 660 ± 10 | 680 ± 10 | 610 ± 20 | 620 ± 0 | 530 ± 10 | 570 ± 10 |
| 96 hr | 640 ± 30 | 570 ± 20 | 570 ± 10 | 570 ± 20 | 520 ± 0 | 510 ± 20 |
| 0.1M NaIO ₄ | | | | | | |
| 0.5 hr | 1530 ± 40 | 1720 ± 30 | 1380 ± 50 | 1310 ± 30 | 620 ± 0 | 630 ± 20 |
| 1 hr | 1530 ± 40 | 1720 ± 20 | 1140 ± 20 | 1070 ± 30 | 420 ± 20 | 470 ± 0 |
| 2 hr | 1810 ± 170 | 1640 ± 280 | 1330 ± 160 | 1020 ± 80 | 380 ± 0 | 400 ± 20 |

Table 3. Calculated chain breaks following alkaline treatment

| | Chain Breaks (mmol/100 g cellulose) | | | | | |
|-----------------------------------|-------------------------------------|---------------|---------------|---------------|---------------|---------------|
| | pH8.5 | | pH10 | | pH12.5 | |
| | 20 min. | 60 min. | 20 min. | 60 min. | 20 min. | 60 min. |
| Unoxidized | | | | | | |
| W1 Control | 0.013 ± 0.001 | 0.039 ± 0.004 | 0.035 ± 0.003 | 0.063 ± 0.010 | 0.047 ± 0.003 | 0.047 ± 0.005 |
| Oxidized | | | | | | |
| UV-A light | | | | | | |
| 2520 hr | 0 | 0 | 0.007 ± 0.001 | 0 | 0.098 ± 0.009 | 0.074 ± 0.006 |
| 6720 hr | 0.006 ± 0.000 | 0.020 ± 0.001 | 0.033 ± 0.001 | 0.047 ± 0.001 | 0.141 ± 0.003 | 0.149 ± 0.003 |
| 10% H ₂ O ₂ | | | | | | |
| 1 hr | 0 | 0 | 0 | 0 | 0 | 0.231 ± 0.016 |
| 24 hr | 0.055 ± 0.003 | 0 | 0.208 ± 0.014 | 0.176 ± 0.010 | 0.514 ± 0.032 | 0.350 ± 0.021 |
| 96 hr | 0 | 0.037 ± 0.001 | 0.037 ± 0.001 | 0.037 ± 0.001 | 0.245 ± 0.004 | 0.292 ± 0.012 |
| 0.1M NaIO ₄ | | | | | | |
| 0.5 hr | 0.143 ± 0.005 | 0.054 ± 0.002 | 0.231 ± 0.010 | 0.278 ± 0.010 | 1.33 ± 0.04 | 1.30 ± 0.05 |
| 1 hr | 0.186 ± 0.007 | 0.097 ± 0.003 | 0.463 ± 0.014 | 0.534 ± 0.020 | 2.32 ± 0.12 | 2.01 ± 0.05 |
| 2 hr | 0.036 ± 0.004 | 0.106 ± 0.020 | 0.282 ± 0.040 | 0.564 ± 0.061 | 2.60 ± 0.19 | 2.44 ± 0.22 |

1994). The greater the number of chain breaks, the weaker the paper became as a result of the alkaline treatment. Previously it was shown that cellulose became extremely weak when the DP fell below 400–600 (Jerosch et al. 2002; Smith 2004; Stephens et al. 2008a). In Eq. 1, substituting the starting $DP_0 = 2760$ and $DP_t = 600$ for the W1 in this study, it is estimated that greater than 1.6 mmol chain breaks/100g cellulose would cause the unoxidized Whatman 1 control to become permanently weak.

Table 3 summarizes the calculated chain breaks after oxidation (DP_0) and following alkaline treatment (DP_t) of each sample in the study. When the average DP of a sample after both oxidation and alkaline treatment was higher than the average DP of its merely oxidized counterpart, a negative value for chain breaks was calculated. This implied that the molecules had gotten longer not shorter during alkaline treatment. However, by taking into account the error in the measurements, with only one exception (10% H₂O₂ 96 hr

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Table 4. Effect of alkaline treatment on DP

| | pH8.5 | | pH10 | | pH12.5 | |
|-----------------------------------|---------|---------|---------|---------|---------|---------|
| | 20 min. | 60 min. | 20 min. | 60 min. | 20 min. | 60 min. |
| UV-A light | | | | | | |
| 2520 hr | - | - | - | - | + | + |
| 6720 hr | - | - | + | + | + | + |
| 10% H ₂ O ₂ | | | | | | |
| 1 hr | - | - | - | - | - | + |
| 24 hr | - | - | + | + | + | + |
| 96 hr | - | - | - | - | + | + |
| 0.1M NaIO ₄ | | | | | | |
| 0.5 hr | + | + | + | + | + | + |
| 1 hr | + | + | + | + | + | + |
| 2 hr | - | - | + | + | + | + |

+ treatment caused measurable damage

- treatment did not cause damage

pH8.5 20), the measured DPs before and after alkaline treatment were found to be the same. Therefore, when the calculated number of chain breaks was negative, it was assumed that no reaction had occurred and a zero was entered into table 3. The 10% H₂O₂ 96 hr pH8.5 20 sample was also given a value of zero because it was deemed unlikely that this sample would have undergone cross-linking while all the other samples in the data set either didn't react at all or underwent β -elimination degradation.

Figure 4 plots the number of chain breaks for samples treated for 60 minutes in one of the three different pH Ca(OH)₂ treatment baths. Figure 4a shows the results from samples oxidized using UV-A, figure 4b the results from samples oxidized in 10% H₂O₂, and figure 4c the results from samples oxidized using 0.1M NaIO₄. Qualitatively, the results show that the UV-A oxidized samples were virtually unaffected by alkaline treatment while the H₂O₂ oxidized samples were slightly sensitive to degradation at pH 12.5. The NaIO₄ oxidized samples were increasingly sensitive to degradation with increasing pH.

Precise statements regarding whether or not alkaline treatment baths were damaging to oxidized papers were made possible by a statistical analysis of the GPC results. A 2-sample Student's *t*-test analysis was used to determine if the DPs of oxidized samples before and after alkaline treatment were the same, implying no damage had occurred, or different, implying the treatment bath was damaging (Brase and Brase 1995; Stephens et al. 2008b). Table 4 summarizes the outcome of the analysis: a plus sign indicates the alkaline treatment bath caused measurable damage to the ox-

idized cellulose in the paper; a minus sign indicates alkaline treatment baths did not cause any damage to the cellulose.

Results showed that at pH 8.5, the UV-A and 10% H₂O₂ oxidized samples were unaffected by the alkaline treatment baths. Hence, this pH did not cause β -elimination reactions during treatment of up to one hour at RT. For the NaIO₄ oxidized samples, four of the six samples were found to be sensitive to β -elimination reaction. However, the number of chain breaks that occurred was relatively small in comparison to the measured carbonyl content of the samples. This pH was too low to cause major alkaline degradation during treatment of up to one hour at RT.

When the pH was increased to 10.0, the sensitivity of the UV-A and 10% H₂O₂ oxidized samples to β -elimination degradation was inconsistent. The UV-A 6720 hr and 10% H₂O₂ 24 hr samples were sensitive to degradation while the other three sets of samples were not. The 10% H₂O₂ 1 hr samples, which were less oxidized than the UV-A 6720 samples, may not have had enough oxidized sites to cause a measurable change in DP when placed in the pH 10.0 bath for up to an hour. Regardless, for the samples that were found to be sensitive to degradation, the amount of degradation that occurred was minimal. It was concluded that samples oxidized using UV-A light or H₂O₂ were not particularly sensitive to degradation at pH 10.0. By contrast, all of the NaIO₄ oxidized samples were somewhat degraded in pH 10.0 baths.

At pH 12.5, nearly all samples, regardless of the type of oxidation, were statistically determined to be sensitive to β -elimination reactions. The UV-A

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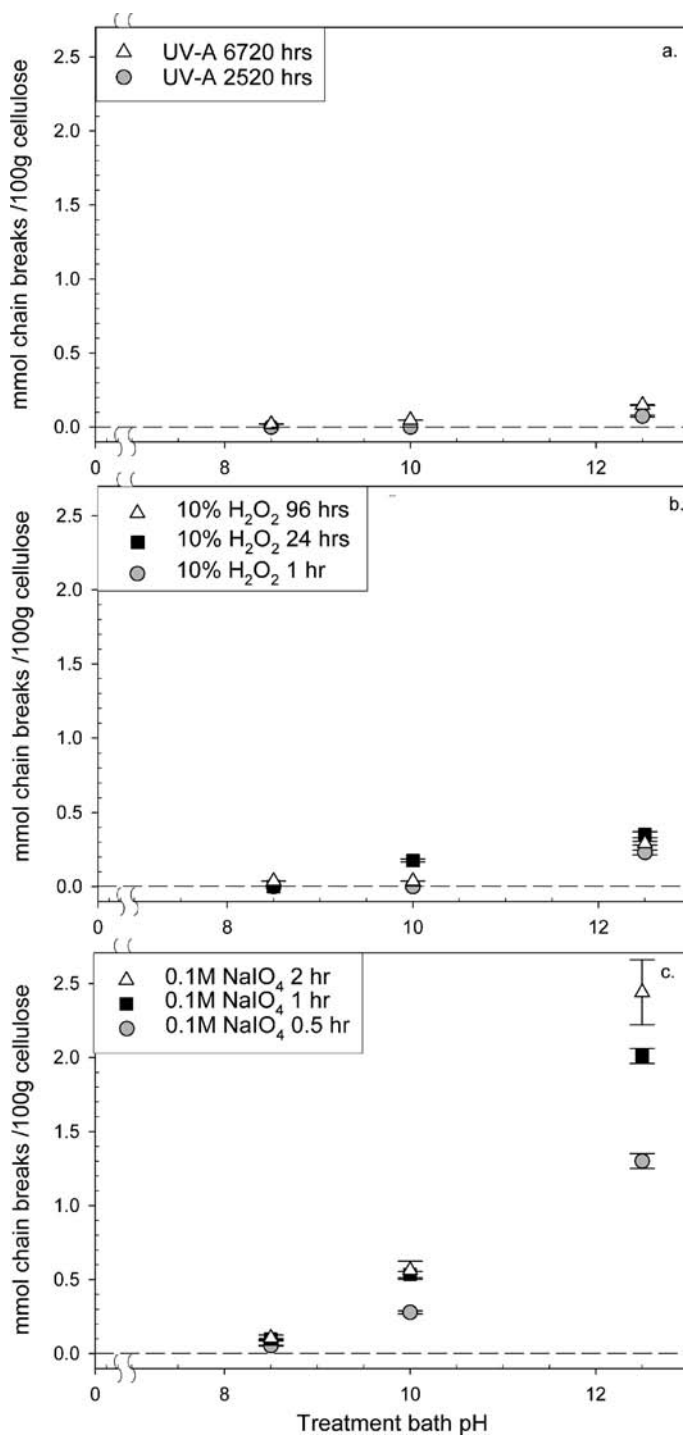


Fig. 4. Chain breaks as a function of 60 min. calcium hydroxide treatment baths; paper oxidized by (a) UV-A, (b) 10% hydrogen peroxide, (c) 0.1M sodium metaperiodate

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samples (fig. 4a) were only slightly sensitive: the greatest amount of degradation observed was on the UVA 6720 hr pH12.5 60 sample (table 3), in which the 0.149 mmol chain breaks/100g cellulose observed is ten times less than would be required to render the paper extremely weak. The H₂O₂ samples (fig. 4b) were more sensitive to degradation than the UV-A samples, with the 10% H₂O₂ 24 hr pH12.5 20 sample showing the most degradation at 0.514 mmol chain breaks/100g cellulose (table 3).

The NaIO₄ oxidized samples (fig. 4c) were extremely sensitive to degradation at pH 12.5. As shown in table 3, the degradation of the NaIO₄ oxidized samples was between five and fifty times greater than the degradation observed in the UV-A and 10% H₂O₂ oxidized samples. For 0.1M NaIO₄ 1hr and 2hr samples, regardless of treatment time, treatment in the pH 12.5 Ca(OH)₂ solution rendered them permanently weak, while the samples oxidized for 0.5 hr were significantly weakened.

While the 10% H₂O₂ 96 hr and 0.1M NaIO₄ 0.5 hr samples were oxidized roughly the same amount (based on carbonyl content analysis), results showed that the NaIO₄ oxidized samples underwent more degradation at pH 10.0 and 12.5 than the H₂O₂ oxidized samples. The explanation for this lies in the location of the carbonyl groups formed during the two different oxidation reactions. When samples underwent H₂O₂ oxidation, roughly one third of the reactions caused carbonyls to be located at the chain ends of the cellulose molecules (Whitmore and Bogaard 1994). Carbonyls at chain ends undergo peeling reactions, not β -elimination reactions, when placed in alkaline environments (Potthast et al. 2006). Peeling reactions cause insignificant changes to the molecular weight because only one DP unit is lost in each reaction. Conversely, when samples were oxidized using NaIO₄, the reaction placed a majority of the carbonyl groups along the cellulose chain, setting up the molecule for large reductions in molecular weight should reactions occur in alkaline solution.

The findings in this study with respect to periodate-oxidized samples are in good agreement with results reported in the literature. Davidson (1940) also saw that at room temperature, periodate oxidized cellulose was extremely sensitive to degradation by using sodium hydroxide solutions at pH12.7. O'Meara and Richards (1958) also observed a similar sensitivity of periodate oxidized cellulose to degradation by oxygen-free lime water, i.e., saturated Ca(OH)₂, pH = 12.5.

Table 5. Effect of treatment time on degradation

| | pH8.5 | pH10 | pH12.5 |
|-----------------------------------|-------|------|--------|
| UV-A light | | | |
| 2520 hr | | | + |
| 6720 hr | | + | + |
| 10% H ₂ O ₂ | | | |
| 1 hr | | | |
| 24 hr | | + | + |
| 96 hr | | | - |
| 0.1M NaIO ₄ | | | |
| 0.5 hr | + | + | - |
| 1 hr | + | + | + |
| 2 hr | | + | - |

+ treatment time affected degradation

- treatment time had no effect

5.2 EFFECT OF TREATMENT TIME ON β -ELIMINATION REACTIONS

The effect of treatment bath time on the extent of β -elimination reactions was examined. Only samples that were determined to be sensitive to degradation at both treatment times were analyzed. Table 5 summarizes the results of a 2-sample Student's *t*-test that determined if there was a difference between two samples oxidized the same amount but soaked for different lengths of time at the same pH; a plus sign indicates that treatment time affected degradation, a minus sign indicates that no effect of treatment time was found. Results showed that eleven of the fourteen sample sets showed an effect of treatment time. It was therefore concluded that soaking samples for longer time generally caused more damaging β -elimination reactions to occur. Hence, at RT and high pH, maintaining shorter treatment times will tend to avert some of the possible β -elimination reactions.

6. CONCLUSIONS

At the beginning of this study, it was thought that alkaline treatment baths of oxidized cotton paper would be damaging, i.e., that alkaline baths would decrease the molecular weight, and hence the strength, of cellulose through β -elimination reactions. It was not known to what extent the type of oxidation, pH level, or treatment time would affect degradation.

Results from this study showed that the type of oxidation used to create carbonyl groups along the cellulose chain affected its sensitivity to degradation.

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Samples oxidized with NaIO_4 were particularly sensitive to alkaline degradation, especially at pH 12.5. This oxidation method opened up the anhydroglucose ring and placed carbonyl groups at locations on the cellulose chain that left it vulnerable to β -elimination reactions when exposed to alkaline environments.

For samples oxidized in a manner that mimicked oxidation occurring in nature or during conservation treatment—namely UV-A and H_2O_2 oxidation—little alkaline sensitivity was observed for treatments at pH 10.0 or lower. Even at pH 12.5 these papers degraded only very slightly. The most damage to the UV-A and H_2O_2 oxidized papers occurred during the oxidation step itself.

Regardless of the mode of oxidation, there was no conclusive evidence showing that an increased level of oxidation led to an increased sensitivity to alkaline degradation. More work is necessary to clarify this issue. However, it was observed that for the papers that were sensitive to alkaline degradation, shortening the treatment time served to decrease the damage incurred. It is not known whether the degradation observed during the course of these experiments was the greatest amount possible, or whether even longer treatment times would have led to greater numbers of chain breaks.

Since it is unlikely that an art object will have been subjected to sodium metaperiodate exposure, the results from this study suggest that $\text{Ca}(\text{OH})_2$ baths up to and including pH 10.0 can be considered safe for conservation treatments of paper. Of course, only risks to the cellulose component of the paper were tested. Before any conservation treatments are undertaken, the effect of pH and $\text{Ca}(\text{OH})_2$ on the media, sizing, and any other components of the paper must also be considered. Future examination of high pH treatments (pH 12.5) will compare the disadvantages of slightly damaging cellulose during alkaline treatment to the beneficial effects of increasing the pH of the paper, which would serve to slow cellulose hydrolytic degradation in the future.

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SOURCES OF MATERIALS

Whatman grade no. 1 qualitative filter paper,
catalog no. 1001 917
Whatman
Building 1
800 Centennial Avenue
Piscataway, NJ 08854
<http://www.whatman.com>

Hydrogen peroxide, puriss grade, unstabilized
30%, Fluka catalog number 95313
Calcium hydroxide, Aldrich catalog number
23,923-2

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Hydrazine dihydrochloride, Sigma-Aldrich catalog number 216208

Lithium chloride, Sigma-Aldrich catalog number 310468

p-dimethylaminobenzaldehyde, Sigma-Aldrich catalog number 156477

Fluka, Aldrich, Sigma-Aldrich
3050 Spruce St.
St. Louis, MO 63103
<http://www.sigmaaldrich.com>

Sodium metaperiodate, catalog no. S-398

Sulfuric acid, catalog no. A300SI-212

Methanol, catalog no. A452SK

Fisher Scientific

81 Wyman St.

Waltham, MA 02454

<http://www.fishersci.com>

Dimethylacetamide, catalog no. HP562

Spectrum Chemicals

755 Jersey Ave.

New Brunswick, NJ 08901

<http://www.spectrumchemical.com>

Pullulan standards, catalog no. WAT034207

Waters

20 Liberty Way

Franklin, MA 02038

<http://www.waters.com>

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