Investigating the combination of hydrogen peroxide and tetraacetylethylenediamine (TAED) for use in paper bleaching

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Abstract

In paper conservation chemical bleaching is considered a cosmetic procedure to remove or diminish disfiguring stains present on the object. However, it is difficult to confine the action of the bleach to the stains, and the components that make up the object may also be changed or damaged. Of all the bleaches available, an alkaline solution of hydrogen peroxide is considered the best oxidative bleaching agent because of its low impact on the cellulose substrate.

This research investigates the use of the activator tetraacetylethylenediamine (TAED) in conjunction with hydrogen peroxide. TAED is currently used in the paper industry in the bleaching of pulp. Literature from the paper industry suggests that its inclusion in the bleaching process has distinct advantages over the use of hydrogen peroxide alone, especially in terms of pH tolerance, bleaching efficiency and retention of fibre strength. The objective of the work described here is to explore the possibility of using this activator in paper conservation. Tests were made using alkaline solutions of hydrogen peroxide with and without TAED, and analysis of the results shows that the presence of TAED enhances the bleaching effect and might allow bleaching to be performed at neutral pH conditions.

Introduction

Paper is a composite material whose chief constituent is cellulose. As a general rule paper discolours and becomes brittle as it ages, either through the action of unstable components of the paper or through the effects of environmental factors such as pollution and light exposure. Sometimes this discolouration can detract from the visual appearance of the object. When this happens, conservators consider various treatment approaches in order to minimise the problem. Possible treatments include washing, alkaline baths, solvent treatments, enzyme treatments and bleaching. Among them bleaching is often considered the last resort because of its potentially harmful effects. Usually bleaching only has an aesthetic function and is not considered essential for conservation of the object.

Bleaching involves both chemically altering the stains from coloured to colourless and solubilising and removing stains from the material. However, it is difficult to confine these changes to the stains and normally the other components of the object may also be changed or damaged by the same reactions. Attention to the method of application and the chemicals used are important in order to make this treatment as 'safe' as possible.

Ethical issues regarding this kind of treatment may relate to such factors as historical concerns, artist's intent and aesthetics. The historical relevance of the stain should be considered prior to intervention. In some cases leaving the obtrusive stain on the object can be visually disturbing, but may be the most ethical option.

There are two kinds of chemical bleaching agents: oxidising and reducing. Both kinds have been used for some time in conservation and the general parameters for their safe use are considered to be well defined. Of all the bleaches used, an alkaline solution of hydrogen peroxide is considered the best oxidative bleach available because it is one of the least damaging to the cellulose (Lienardy and van Damme 1988).

Hydrogen peroxide has been widely used in the paper pulp and textile industries for bleaching. However, this oxygen-releasing material has its drawbacks. Its effectiveness is dependent on high pH conditions, high temperature and long treatment times, all of which are extremely detrimental to fibre strength and quality.

In recent times in the paper industry, peroxide bleaching has incorporated the use of a 'bleaching booster', tetraacetylethylenediamine (TAED). Use of TAED has been shown to produce a stronger oxidative bleaching effect, allowing for bleaching at lower temperatures and less alkaline conditions (Turner and Mathews 2004: pp 1–8). This allows for a satisfactory bleaching effect while reducing the loss in fibre strength usually associated with bleaching (Shangyuchem 2003).

This paper will discuss the possibility of using a TAED activator in paper conservation bleaching. It will also discuss the possibility of establishing a less detrimental methodology for bleaching by:

- investigating the possibility of achieving a satisfactory bleaching effect using low-concentration solutions of hydrogen peroxide with added TAED
- exploring the possibility of undertaking satisfactory bleaching, in the presence of TAED, at neutral pH
- verifying the possibility of using more effective mild (less alkaline) bleaching solutions or shorter retention times in combination with TAED.

Finally, this paper does not support the regular use of bleaching in conservation for reducing discolouration. It is widely accepted that bleaching should only be considered as a last option for reducing unwanted stains that interfere with the visual integrity of an object.

Method

The paper used in this study was taken from the book *Historia de la creacion de los seres organizados segun las leis naturales*, printed in 1906. This particular book was chosen due to its age, condition and high degree of discolouration, which are important factors in this kind of treatment.

The research was developed using three experimental trials:

Experiment I

- Group I: 5% H_2O_2, pH = 9 (made alkaline with ammonia), 30 minutes, room temperature.
- Group II: 5% H_2O_2 + 2% TAED, pH = 9 (made alkaline with ammonia), 30 minutes, room temperature.
- Group III: 5% H_2O_2 + 2% TAED, pH = 7 (made neutral with ammonia), 30 minutes, room temperature.
- Group IV: 5% H_2O_2 + 2% TAED, pH = 9 (made alkaline with ammonia), 15 minutes, room temperature.

Experiment II

- Group V: 3% H_2O_2, pH = 9 (made alkaline with ammonia), 30 minutes, room temperature.
- Group VI: 3% H_2O_2 + 2% TAED, pH = 9 (made alkaline with ammonia), 30 minutes, room temperature.
- Group VII: 4% H_2O_2 + 2% TAED, pH = 9 (made alkaline with ammonia), 30 minutes, room temperature.

Experiment III

- Group VIII: 3% H_2O_2 + 2% TAED, pH = 7 (made neutral with ammonia), 30 minutes, room temperature.

All experiments were carried out following the same basic procedures:

1. Pages from the book were selected randomly and analysed. They were subjected to a series of spot tests and analysed for their pH and their internal tear resistance. Their colour was measured and they were analysed using Fourier Transform Infrared Spectroscopy (FTIR). Test procedures are described in the following section.
2. Pages were divided into sections and each section subjected to a different treatment. For each Group (Group I–Group VII), five replicates were made in order to ensure statistically significant results.
3. All samples were first alkaline washed for one hour in a calcium hydroxide solution (pH = 8.5). The alkaline solution was changed after 30 minutes. They were dried between blotters and felts under light pressure.
4. Samples were then immersion bleached using the different solutions. All bleaching solutions were prepared in a fume cupboard in the following manner: First, the hydrogen peroxide solution was prepared and the pH adjusted to the desired level. Then half of the solution was mixed with TAED and agitated for approximately 10 minutes using a magnetic stirrer. It was found that froth developed on the surface while mixing the solution with TAED; this froth was skimmed from the solution before mixing with the rest of the original solution. Finally, the pH of the final solution was measured and adjusted if necessary.
5. Following bleaching all samples were washed in deionised water for one hour, the water being changed after 30 minutes. Following this, the

samples were again alkaline washed for 30 minutes in a calcium hydroxide solution (pH = 8.5).

6. All samples were re-examined for changes in pH, colour profile, internal tear resistance and FTIR results. This analysis was intended to determine any changes that occurred as a result of the different treatments.

In order to simulate the long-term effects of the treatments, bleached samples from Experiments I and III were artificially aged and then resubmitted to the same analysis described above. Samples from Experiment II were not submitted to artificial aging due to time constraints. Artificial aging was carried out by placing the samples in an oven (Qualtex Solidstad) with a dry atmosphere at 105°C for a period of two weeks.

Testing procedures

Spot tests

Sample papers were subjected to a series of analyses to detect the presence or absence of specific materials. The analysis included spot tests for lignin, starch, protein, carbonates and rosin.

pH

Cold extraction was chosen to measure the acid content of the samples before and after treatment. The procedure followed the methodology standardised by the Technical Association of the Paper and Pulp Industry (TAPPI).

Internal tearing resistance

Internal tearing resistance was measured using an Elmendorf internal tearing tester 1653, with a 'C' pendulum, in accordance with TAPPI Standard T 402om-83. The tearing tester was manufactured by Messmer-Buchel. Since mechanical strength is greatly influenced by the moisture content of the samples, careful attention was given to proper sample conditioning as per TAPPI Method T 402sp-03: Standards conditioning and testing atmospheres for paper, board, pulp handsheets and related products.

Colour measurement

Colour measurements were made with a Minolta Spectrophotometer CM-3600 d using the CIE L*a*b* colour notation system. Five measurements, at exactly the same location, were taken from each sample before and after each bleaching treatment. The results were averaged and their standard deviations and coefficient of variation were calculated in order to determine the precision of the results.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out with a Thermo Nicolet Nexus instrument utilising an attenuated total reflection stage. FTIR was undertaken in the same location on the samples before treatment, after bleaching and after aging.

Results and discussion

Spot tests

Of the five materials tested for, only lignin was detected. The presence of lignin, along with the brittle and yellowed appearance of the pages, indicated that the samples were predominantly composed of wood-pulp fibres. Since papers of this make-up are often subjected to bleaching treatments in libraries and archives it was felt that they were an ideal test subject to examine the effects of TAED-assisted bleaching.

pH

The results of the pH testing showed that all treatments resulted in an improvement in the pH of the papers. Of particular interest was the finding that the final pH of the papers was much the same whether they had been simply alkaline washed, or bleached, rinsed and then alkaline washed. This suggests that the main determinant of the final pH of the bleached samples was not the high pH used in the majority of the bleaching solutions but the extensive rinsing and alkaline washing after bleaching. The slightly higher pH of the samples bleached with 3% hydrogen peroxide solutions may be related to the mild concentration of hydrogen peroxide used in these experiments, which produces a lower concentration of H^+ ions when compared with more concentrated solution (Burgess n.d.). The pH values of the samples both before and after bleaching and washing treatments are plotted in Figure 1.

Internal tear resistance

Changes in a paper's mechanical strength properties are often used to indicate the effects of a treatment on the physical and chemical properties

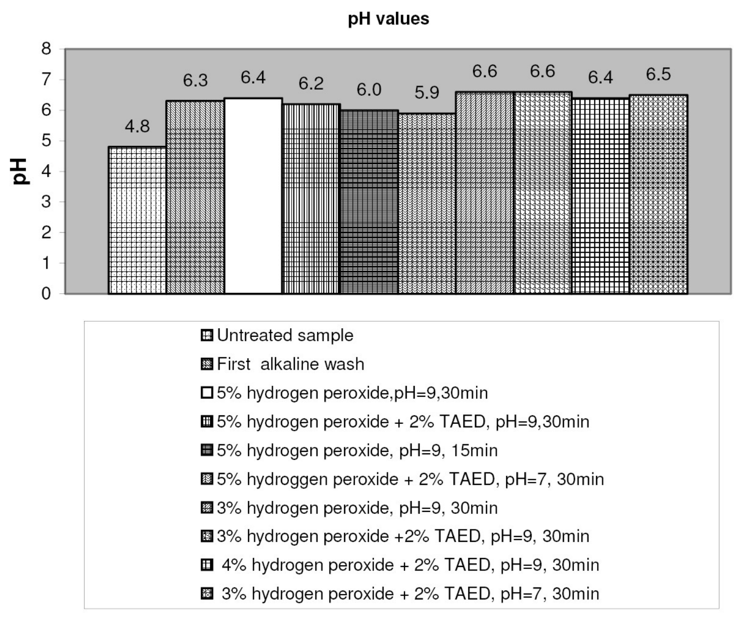

Figure 1. pH values of the samples before and after bleaching.

of the paper. Mechanical strength is commonly measured by one of three methods: folding endurance, tensile strength or internal tearing resistance. To ensure strength tests are as accurate as possible it would have been preferable to carry out all three tests on samples. However, due to the lack of time, samples and equipment, only internal tearing resistance tests were performed in this research.

It has been demonstrated that physical properties of paper can be correlated with the degree of polymerisation (DP), which itself has a direct effect upon the structure of the fibres (Reyden 1992). However, the correlation between retention of physical properties and fibre degradation is not linear and so physical tests can only give an indication of the effects of conservation treatments on fibre strength.

Results showed an increase in the internal tear resistance of all samples after alkaline washing and bleaching. Internal tearing values were observed to be even higher on samples that were treated at neutral pH or those only bleached for 15 minutes, which emphasises the need for an investigation of new bleaching treatments that could be performed under these mild conditions.

The literature states that the presence of TAED in bleaching solutions improves the strength properties of the paper when compared with samples treated by traditional methods (Warwick International 2004). However, this result was not observed in this project. In most cases, the improvement in internal tearing resistance of samples bleached with TAED proved to be similar or smaller than that obtained using traditional methods; the only exceptions were those samples treated under neutral conditions and those bleached for only 15 minutes.

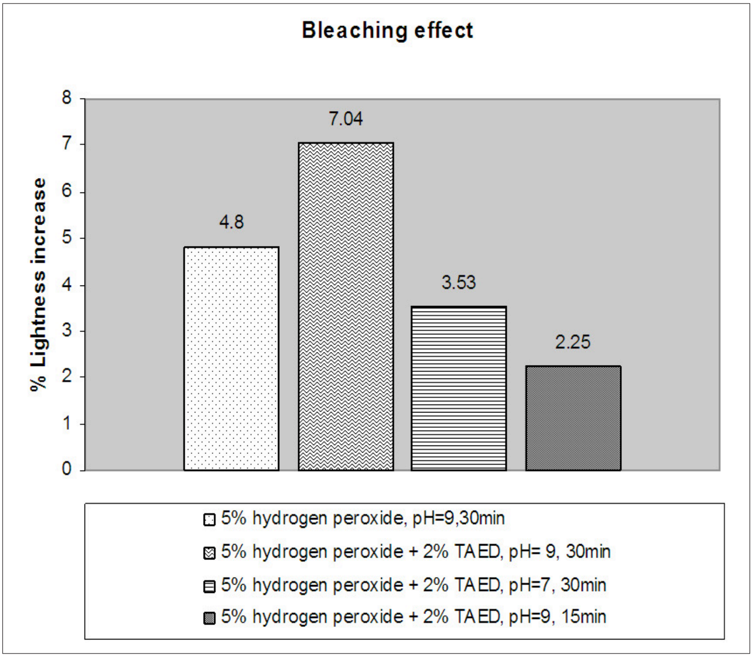

Figure 2. Percentage lightness increase – Experiment I.

Since the presence of ink can affect the internal tearing results, it is advisable to avoid printed samples. Unfortunately this was impossible to achieve since the project aspired to test real samples. Furthermore, degraded papers are likely to be more oxidized near the edges, and some samples used during the tests come from the edge of leaves. Therefore, these factors could have influenced the accuracy of the results and so the use of TAED in bleaching solutions should be investigated in further studies.

Colour measurements

Bleaching treatments are applied in conservation to bring about an improvement in the visual appearance of an object. The efficiency of a bleaching treatment can be quantified by comparing colour measurements of the samples before and after treatment.

Experiment I

From Figure 2 it is possible to compare the bleaching efficiency of the four bleaching solutions used in the first experiment and point out the following observations:

1. The presence of TAED in alkaline conditions increased the bleaching effect.
2. The presence of TAED enabled bleaching to be undertaken in neutral conditions. Although the result under neutral pH was lower than the result obtained when hydrogen peroxide was used alone under alkaline conditions, it can still be considered satisfactory. In similar conditions hydrogen peroxide alone is almost totally ineffective, since an alkaline environment is necessary for hydrogen peroxide to initiate the production of the oxidant species responsible for bleaching.
3. Potentially, the use of TAED could mean that desirable bleaching can be achieved in less time. This suggests that if bleaching is locally applied or undertaken using an immersion method, fewer applications would be necessary or treatment times could be shorter, thus reducing the detrimental effects of bleaching on the paper.

Experiments II and III

The increase in lightness obtained using 5% solution of hydrogen peroxide, pH = 9, for 30 minutes was compared with the increase in lightness

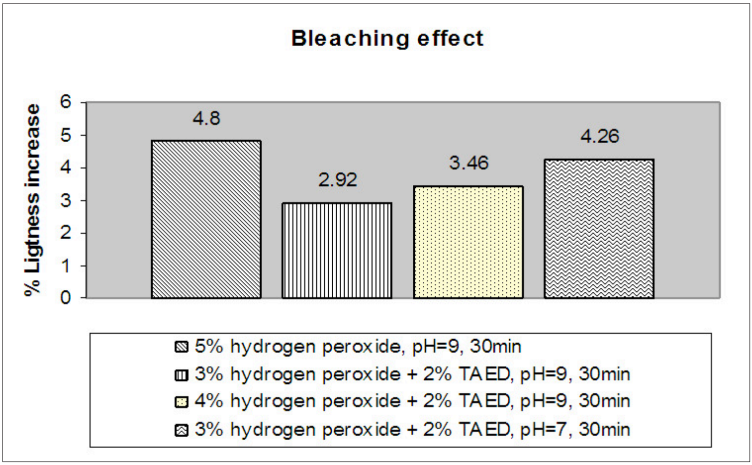

Figure 3. Percentage lightness increase – Experiments II and III.

obtained using 3% and 4% hydrogen peroxide solutions in the presence of TAED. The percentage lightness increase of all solutions is shown in Figure 3.

From Figure 3 it can be seen that the bleaching effect of the 3% and 4% solutions of hydrogen peroxide with TAED under alkaline conditions showed a smaller increase in lightness than 5% hydrogen peroxide alone. Otherwise, the lightness increases of samples treated with 3% hydrogen peroxide with TAED at neutral conditions are very similar to those obtained by samples bleached with 5% hydrogen peroxide alone. These results indicate that the presence of TAED allows bleaching to be performed using low-concentration solutions.

The bleaching solution made with 3% hydrogen peroxide + 2% TAED, pH = 9, for 30 minutes showed a smaller lightness increase than the bleaching solution made with 5% hydrogen peroxide alone. This result was unexpected since the results obtained from Experiment I showed that the presence of TAED in alkaline medium increases the bleaching effectiveness. This may indicate that the efficiency of TAED in alkaline conditions can be related to the molar ratio between TAED and hydrogen peroxide.

The bleaching effectiveness of 3% hydrogen peroxide + 2% TAED at neutral pH was higher than the results obtained when 3% and 4% solutions of hydrogen peroxide were combined with TAED in alkaline conditions. Again, this result was unexpected when compared to the results obtained in Experiment I and may indicate that, depending on the molar ratio between TAED and hydrogen peroxide, the bleaching effect of TAED may be more effective in either neutral or alkaline conditions.

As stated in the literature, the extent of chemical fibre degradation decreases as the pH of the bleaching solution is reduced (Burgess and Hanlan 1980). Therefore the possibility of successfully bleaching at neutral pH would be considered advantageous as it could reduce fibre damage during bleaching. The concentration of the bleach bath also affects the extent of chemical fibre degradation. The literature describes the extent of degradation as a function of concentration and shows that by lowering the concentration of the bleaching solution it is possible to reduce the fibre damage of cellulose materials, especially when less alkaline conditions are used (Burgess and Hanlan 1980).

Accelerated aging using dry heat

Dry heat can be used to accelerate the natural aging of paper. Although imperfect, accelerated aging tests using dry heat are often used to predict how a paper may age. It is also used to compare the effects of different treatment methods on the long-term stability of paper through the comparison of aging results. Accelerated aging was only undertaken on samples from Experiment I.

Hydrolysis and oxidation are the main chemical reactions that take place during paper aging. The yellowing of paper is directly related to the oxidation of cellulose and the formation of carbonyl groups such as aldehydes, ketones and carboxylic acids. Other components present in the paper such as fillers, lignin and hemicellulose are also subject to oxidation and contribute to general degradation and colour formation (Burgess 1982).

During aging these chemical reactions cause colour changes in the paper. Since increased yellowing of the paper can indicate formation of degradation products and chromophore groups (e.g. C=C, C=O) (Burgess

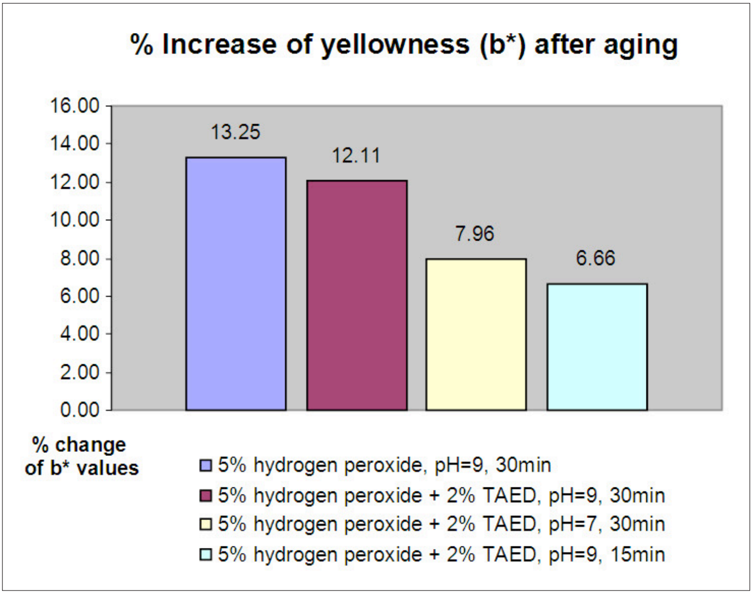

Figure 4. Percentage of b* values increase after aging.

1982), colour measurements can be used to determine the extent of fibre deterioration.

The results of the colour measurements showed that the aged samples that had been treated with hydrogen peroxide alone exhibit higher Δb* (degree of yellowing) than aged samples that had been treated with bleaching solutions containing TAED. The percentage of yellowness increase of the aged samples is shown in Figure 4.

The increased yellowness in the paper after aging can be associated with fibre degradation caused by bleaching (Burgess 1982). It is feasible that samples treated with solutions containing TAED, particularly those at neutral pH and those used with shorter bleaching treatments, underwent less fibre degradation during aging. The oxidation reactions responsible for the generation of carbonyl groups that are strictly related to fibre deterioration and yellowing of the paper were probably lower in these conditions. Consequently, it is possible to infer that the bleaching solutions containing TAED may have a less harmful effect on the paper fibres.

The pH results of the samples after aging showed little change from the pH before aging – about 0.1 to 0.2 units less. These results may be associated with chemical changes causing an increase in hydrogen ion concentration during aging.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a valuable analytical tool that allows the identification of organic and inorganic materials. It is one of a number of types of vibrational spectroscopy where molecular vibrations are analysed. In this project FTIR was used to characterise the functional groups present in the samples and their variation after each bleaching treatment. In particular, FTIR can show the presence of carboxyl and carbonyl functional groups that are related to cellulose oxidation and consequently degradation.

The spectra from each untreated sample was compared with the spectra from that sample after treatment. This showed noticeable increases in the intensity of the peaks. In general, however, samples that were treated with a mixture of hydrogen peroxide and TAED showed a lower increase in the peaks than samples that were treated with hydrogen peroxide alone, especially in the regions related to acid degradation, carbonyl and carboxyl groups.

By comparing the spectra of samples treated with 5% hydrogen peroxide alone and 3% hydrogen peroxide + 2% TAED in neutral conditions it is possible to observe that the spectra of samples treated with the second solution showed a lower increase in the peaks of functional groups peaks after bleaching (Figure 5). This may therefore be considered a less damaging treatment.

Both solutions showed a similar bleaching effect. This result again suggests that by using TAED bleaching can be undertaken at mild conditions which are less detrimental to the paper fibres.

The FTIR spectra of the aged samples was very similar to the spectra obtained immediately after bleaching. The similarity of the spectra taken from papers treated with the various Experiment I solutions may be an indication that the presence of TAED, in bleaching solutions does not accelerate the degradation of the paper over time. The most visible change

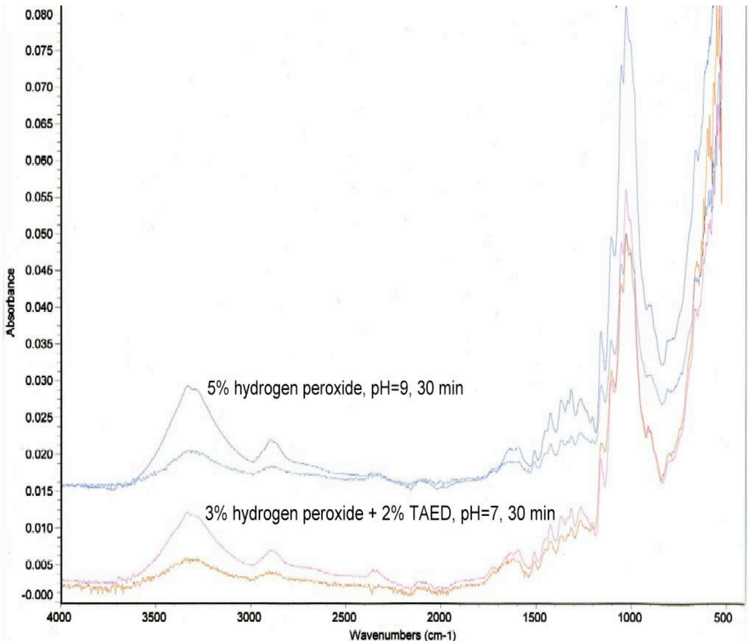

Figure 5 FTIR spectra – before treatment (bottom line) and after bleaching (top line) with two bleaching solutions.

was the decrease in the peak in the O-H region. This change was probably related to the decrease of moisture content of the paper after aging, and to chemical changes that caused an increase in hydrogen ion concentration.

In this project FTIR spectroscopy was used as a preliminary indication of the effect of TAED on cellulose degradation during bleaching. The analysis suggests that, in general, the presence of TAED in bleaching solutions lessens the increase of functional groups that are strictly related to cellulose oxidation, and consequently degradation, when compared with samples treated with hydrogen peroxide alone. However further studies should be undertaken with the objective of precisely determining the extent of cellulose degradation caused by bleaching in the presence of TAED, as well as the increase in carboxyl and carbonyl groups during treatment.

Conclusion

This research investigated the potential for using the activator TAED in hydrogen peroxide bleaching treatments. The results showed that using TAED in bleaching solutions could provide an alternative bleaching technique that is less damaging than most current methods. The main potential advantages are:

- achieving the desired bleaching effect using lower concentrations of hydrogen peroxide
- achieving the desired bleaching effect under neutral pH conditions
- reducing the immersion time required for bleaching.

In comparing the results of samples treated with 5% hydrogen peroxide, pH = 9 for 30 minutes and samples treated with 5% hydrogen peroxide + 2% TAED, pH = 9 for 30 minutes, the bleaching efficiency of the solution with TAED was found to be superior. This is a positive result that suggests that TAED may represent an alternative for attaining satisfactory bleaching using lower retention time, which is less damaging to the paper fibres.

Comparing the results from samples bleached with 5% hydrogen peroxide, pH = 9 for 30 minutes and 3% hydrogen peroxide + 2% TAED, pH = 7 for 30 minutes, shows that in the presence of TAED a desirable bleaching effect can be achieved using a milder concentration of hydrogen peroxide in neutral pH conditions. This can be considered very advantageous as these conditions are known to be less damaging to paper fibres.

The side effects caused by bleaching in the presence of TAED were also examined. In general they were shown to be similar or lower in the activated solutions than in the solutions using hydrogen peroxide alone.

In summary, this research found that in some cases the activation of peroxide through the use of TAED enhances the performance of hydrogen peroxide, increases bleaching efficiency and allows bleaching to be performed in neutral pH conditions. However, wider experimentation is required to further examine the activator's potential effect on paper and its possible use in conservation. There are other important issues to be addressed, such as the question of chemical residues remaining in the paper after bleaching treatments and their potential hazards over time, the most favourable molar ratio between hydrogen peroxide and TAED and the effect of bleaching solutions containing TAED on different types of papers as well as on paper coatings, inks and colourants. This project's conclusions are preliminary and need to be confirmed by further studies.

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