Diffuse reflectance ultraviolet spectroscopic studies of paper

Application Note

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Summary

The diffuse reflectance ultraviolet spectra of papers made from eucalypt chemimechanical pulp have been obtained before and after the pulp was bleached and then after the papers had been exposed to ultraviolet light for four hours. The bleaching agents used, hydrogen peroxide and sodium borohydride, were found to remove bands in the spectra near 370 and 320 nm respectively. These bands probably arise from strongly conjugated C=O and C=C systems such as occur in o-quinones and in aromatic aldehydes, acids and ketones. Exposure to light restored the absorption bands removed by bleaching indicating that the parent groups had been changed but not removed by the bleaching agents.

Introduction

Paper consists of lignocellulose fibers which have been separated from each other by pulping and then reformed into a felted sheet. A number of pulping methods are available giving fibers of widely varying lignin contents whereas more ephemeral products such as newsprint are made largely from mechanical pulps with high lignin contents. Both types of pulp may be bleached to high brightness.

Chemical pulps are obtained in low yields, are more expensive, and require much larger scale processing than mechanical pulps to be economic because of their need for recovery of chemicals. Therefore, the industry is substituting mechanical pulps for chemical pulps in products where lesser properties can be tolerated. However, before this substitution can be extended to further products several disadvantages of mechanical pulps have to be alleviated. One of these is the strong tendency of such pulps to lose brightness and become yellow on prolonged exposure to light.

Paper appears yellow when it contains chromophores which absorb light in the blue-green region. The phenomenon is largely a surface effect (1). Such chromophores are formed by the reactions of groups in lignin with light. The standard industry test for brightness measures the light reflected diffusely at 457 nm. However, the diffuse reflectance spectra of paper can now be measured over a much wider range of wavelengths and give more information concerning the nature of the groups causing lower brightness and color. In this paper we report measurements of the diffuse reflectance ultraviolet/visible spectra of eucalypt chemimechanical pulps bleached with hydrogen peroxide and sodium borohydride. Chemimechanical eucalypt pulps are of interest because they are suitable for making fine printing papers in all aspects except durability.

Experimental

The unbleached and bleached pulps were laboratory samples whose preparation has been described previously (2). Handsheets of basis weight 60 g/m^2 were prepared from the pulps in a British Standard sheet machine with recirculation of the whitewater to minimise the loss of fines.

The brightness of the handsheets was measured at a wavelength of 457 nm with an Elrepho reflectometer calibrated on the basis of MgO-100. Handsheets were irradiated on the wire side in a QUV Accelerated Weathering Tester which contained eight fluorescent FS40 UV tubes. The emitted light was in the wavelength range 280-420 nm with the maximum intensity at 313 nm. The temperature was controlled at 35 °C.

Spectroscopic measurements

The diffuse reflectance spectra of the bleached and yellow sheets were measured on samples of standard handsheets 10 mm x 30 mm by using a Cary 2400 UV-Vis-NIR spectrophotometer fitted with a Cary diffuse reflectance accessory. The spectra were collected in absorbance at a spectral bandwidth of 2 nm and at a rate of 200 nm/min between 260 and 540 nm. For the initial spectrum of Whatman filter paper a reference of pressed PTFE powder was used. As the filter paper spectrum showed little absorption in this region it was itself used as a reference for the other spectra. The spectra have been smoothed and derivatized by using the Savitsky-Golay method (3) employing 25 convolution points.

Results and discussions

The spectra are shown with the ordinate as the difference between the absorbance of the paper sheet comprising the chemimechanical pulp and Whatman No 40 filter paper. This was done to reduce the effect of scattering on the spectra obtained. The resulting absorbance would not be expected to be strictly proportional to the concentration of absorbing species in the sheets but should, nonetheless, provide a useful measure.

Figure 1 shows the absorption of the unbleached and bleached pulps. A dashed line is used to indicate the intercept at 457 nm, the wavelength at which brightness is measured. The values of brightness observed for the various pulps are included in brackets in the captions to the figures. The strongest absorption in each of the spectra in Figure 1 is found near 280 nm. This band is well known in lignin spectra (4). Its intensity is little affected by the treatment with peroxide but appreciably reduced by the treatments involving borohydride. The effects of the bleaching treatments on the spectra can be seen more readily by examining them as differences (Figure 2).

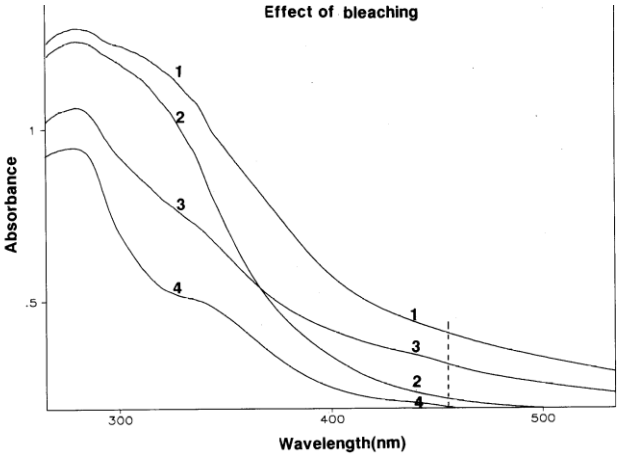

Figure 1. UV-Vis absorption spectra of pulps.
1. Unbleached pulp (Br 53.9)
2. Pulp bleached with hydrogen peroxide (Br 78.8)
3. Pulp bleached with sodium borohydride (Br 66.7)
4. Pulp bleached with hydrogen peroxide and sodium borohydride (Br 87.8)

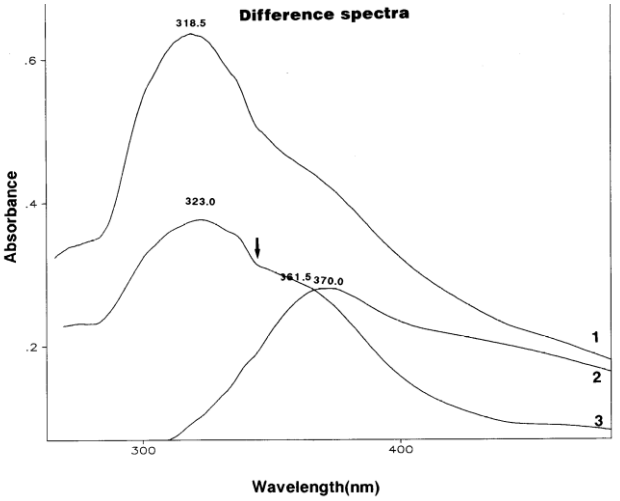

Figure 2. Difference spectra of bleached pulps.
1. Unbleached pulp minus pulp bleached with hydrogen peroxide and sodium borohydride.
2. Unbleached pulp minus pulp bleached with hydrogen peroxide..
3. Unbleached pulp minus pulp bleached with sodium borohydride (Arrow denotes effect of source change.**)**

This shown that the treatments with sodium borohydride remove bands near 320 nm and the treatments with hydrogen peroxide remove bands near 370 nm. The most probable contributors to the band at 320 nm are structures similar to those found in the carbonyl moiety of compounds like coniferaldehyde methylether, sinapic acid methlyether and o-hydroxyacetophenone.

The band found near 320 nm in o-hydroxyacetophenone has been attributed to either a carbonyl n- *transition (5) or to an electron transfer band (96). The most probable assignment of the 370 nm band is to an absorption of an o-quinonoid structure. For example, Imsgard *et al.*(7) found that a polymeric quinone made by oxidizing isoeugenol absorbed at 380 nm. This band has a broad tail into the visible and would certainly be a major contributor to the paper color and its weakening by the hydrogen peroxide treatment a major factor in the improved paper brightness resulting from this treatment.

Figure 3 shows the effect of exposing the unbleached and bleached pulps to ultraviolet radiation for 4 hours. A large increase in absorption is shown by all the pulps with only a small residual benefit of the bleaching treatment evident. The wavelengths of the new absorbing species following light exposure are seen most easily by examining the difference (exposed minus unexposed pulp spectra. These are shown in Figure 4.

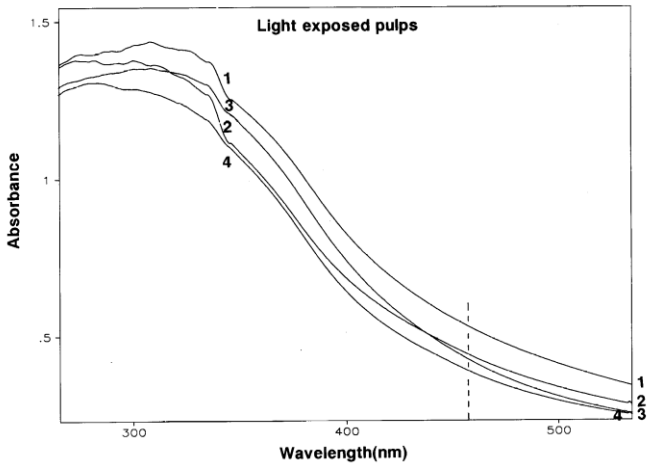

Figure 3. UV-Vis absorption spectra of UV light exposed pulps.
1. Unbleached pulp (Br 42.1)
2. Pulp bleached with hydrogen peroxide (Br 50.2)
3. Pulp bleached with hydrogen peroxide and sodium borohydride (Br 58.0)

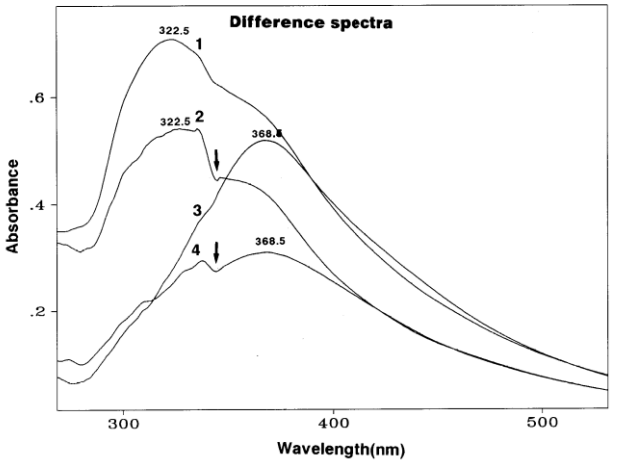

Figure 4. UV-Vis difference spectra of light exposed pulps. Exposed pulp minus unexposed pulp.
1. Pulp bleached with hydrogen peroxide and sodium borohydride.
2. Pulp bleached with sodium borohydride.
3. Pulp bleached with hydrogen peroxide.
4. Unbleached pulp. (Arrows denote mismatch due to source change.)

There are clear differences in the response to light exposure between pulps bleached with hydrogen peroxide and those bleached with sodium borohydride, with the former showing a band near 368 nm and the latter a band 322 nm. These wavelengths are almost the same as those of the bands in Figure 2 shown as having been removed by the respective bleaching treatments. Thus a major effect of the light exposure of pulps bleached by these treatments is to restore absorptions removed by both the oxidative and reductive bleaching treatments suggesting that these treatments have only altered but not removed the groups responsible for the bands.

The bands in the spectra, even of the differences, are very broad. One way of attempting to find whether there is a sub-structure to broad bands is to take the second derivative. Even derivatives of profiles describing spectroscopic band shapes have the same frequency values as ordinary peaks but are much sharper. The potential of this technique has been known for some time but its use has had to wait until spectra with high signal-to-noise ratios were available. The noise level increases with higher derivatives and sets an effective limit to their use.

Figure 5 shows how two overlapping bands can be resolved by using the second derivative mode. The effect of taking the second derivative of the difference spectrum 1 from Figure 4 is shown in Figure 6.

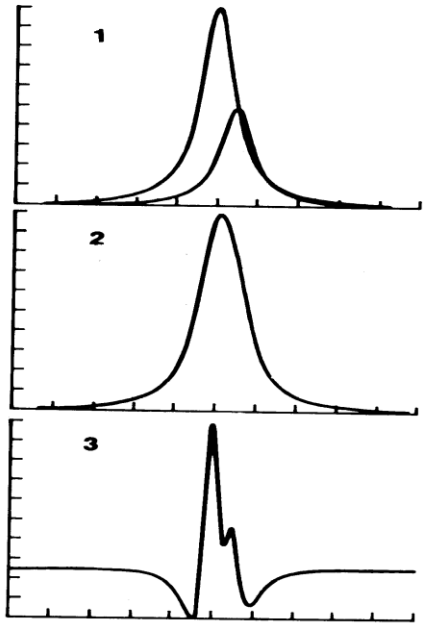

Figure 5. 1. Two adjacent bands.
2. Sum of two adjacent bands.
3. Second derivative of sum of two adjacent bands

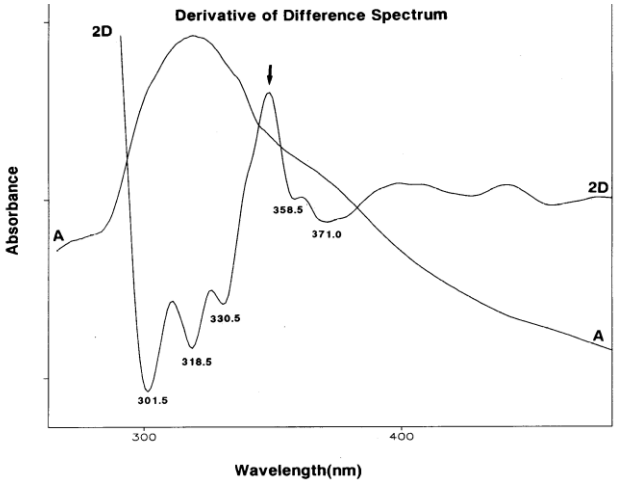

Figure 6. Second derivative (2D) and normal (A) modes of the difference spectrum of light exposed pulp bleached with sodium borohydride and hydrogen peroxide minus unexposed similarly bleached pulp

Here the software has not inverted the derivative so that peaks appear downwards. The derivative spectrum suggests that the 322.5 nm peak is composed of three peaks at 301.5, 318.5 and 330.5 nm and that the shoulder near 368.5 nm may be a doublet. These results are very interesting but some more work needs to be done to prove the validity of the method as has been done for infrared spectra (8).

Conclusions

From the studies we conclude that hydrogen peroxide and sodium borohydride in bleaching the pulps do so by affecting different groups, associated with absorptions near 370 nm and 320 nm respectively. These absorptions are probably derived from conjugated C=O and C=C groups such as occur in o-quinonoid and hydroxy substituted aromatic acetophenone type moieties in the pulp lignin. Although these groups are altered, they are not removed by the treatments and their absorptions are restored when the pulps are exposed to ultraviolet light.

Acknowledgements

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