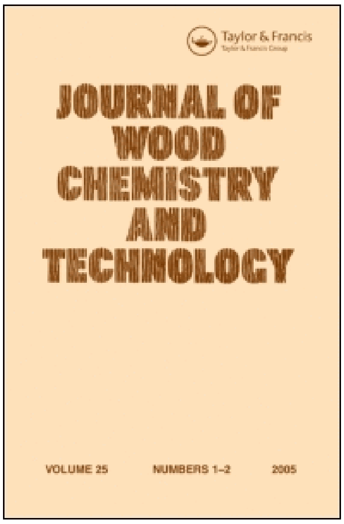

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DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM (DRIFT) SPECTROSCOPIC STUDY OF BLEACHING AND YELLOWING OF EUCALYPT COLD SODA PULP

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ABSTRACT

E. regnans cold soda pulp has been bleached to a high brightness (about 87) in a single-stage treatment with alkaline hydrogen peroxide, and also in 2- and 3-stage sequences which used sodium borohydride in the second stage. The sequences did not provide further appreciable increases in the brightness level, but the borohydride-treated pulp showed greater brightness stability when irradiated with UV light, even when the pulp had been subjected to a third stage hydrogen peroxide bleach.

Chemical changes in the pulps resulting from the bleaching treatments and from their exposure to UV light have been followed by studying the DRIFT spectra (1400-1800 cm^{-1}) of the wire side of handsheets. Variations in band intensity have been related to changes in pulp brightness and to oxidation of the pulps. Some features of the observed variations are not readily explicable.

INTRODUCTION

High yield pulps are being used in increasing quantities throughout the world as components of a wide variety of paper products. One of the obstacles preventing the use of these pulps in high-quality paper is the difficulty of bleaching them to a high brightness which is maintained throughout the lifetime of the product. The tendency for these lignin-containing pulps to yellow on exposure to light is a big disadvantage. The bleaching and brightness reversion of chemimechanical eucalypt pulps was studied as part of a program aimed at preparing high-quality pulp from this wood resource. The pulps used in this study were made by the cold soda process from *Eucalyptus regnans* wood.

One of the difficulties in studying bleaching and yellowing of pulps is that the reactions take place on the surfaces which cannot be readily separated from the bulk of the fibres for chemical studies. However, surfaces can be studied directly by using spectroscopic techniques based on reflection. Infrared spectroscopy, in particular, is well-suited to studies of mechanical pulp bleaching and brightness reversion because it gives direct information about functional groups in the pulps. Until recently, infrared spectroscopy lacked sufficient sensitivity to enable it to be used effectively with reflection sampling techniques. This difficulty has been overcome by using more effective optical arrangements for collecting radiation reflected diffusely from rough surfaces together with new generation Fourier transform infrared (FTIR) instruments. This combination has enabled diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) to become a valuable technique for studying changes in the chemistry of surfaces.[1] Recently St Germain and Gray[2] used an alternative FTIR technique, the photoacoustic technique, to show that a peak ratio method could be used to detect chemical changes in black spruce RMP brightened with hydrogen peroxide. Earlier, the transmission infrared spectra of thin sheets were obtained by Polcin and Rapson[3,4] as part of extensive studies of the effects of brightening western hemlock and eastern spruce groundwood pulps with various chemical treatments.

The DRIFT and photoacoustic methods can be applied to study the surfaces of papers independent of grammage whereas the transmission method requires special thin sheets[3] (20 g/m^2) and may also require incorporation in an alkali halide to reduce scattering. The photoacoustic method yields infrared spectra indirectly and the intensities of bands, unlike bands in normal infrared spectra, are frequency dependent and are not readily quantified[2]. Reflectance values obtained by the DRIFT method need to be converted to relate them to the amounts of absorbing species. This is usually done by using the Kubelka-Munk transformation, which was derived for optically homogeneous sheets, and by assuming that the scattering coefficient varies only slowly with frequency.

EXPERIMENTAL

Pulp Preparation

A sample of woodchips was prepared from five 24 year old *E. regnans* trees. The woodchips were soaked at ambient temperature for 18 h in a sodium hydroxide solution (10 per cent, wood basis) with a liquor to wood ratio of 5:1. The excess liquor was drained from the woodchips which were then refined in a Sunds Defibrator CD300 pilot plant. The refiner was pressurized with compressed air to facilitate collection of the pulp. Two stages of refining were used to prepare pulps with freeness levels of 527 and 318 Csf. The pulps were thoroughly washed with water to remove water-soluble material. The higher freeness pulp was used without further treatment for handsheets from unbleached pulp. The lower freeness pulp was used for the bleaching experiments and was soaked in DTPA solution (0.2 per cent, pulp basis) for 1 h and then washed with purified water prior to bleaching.

Bleaching of Pulps

The pulp was dewatered to a solids content of about 40 per cent in a screw press. The pressed pulp was fluffed in a high-speed Waring blender, mixed with the solution of bleaching chemicals and placed in a plastic bag which was heated in an oven at 50°C for various periods. The conditions for the first stage hydrogen peroxide bleaching were as follows: pulp consistency 30 per cent; sodium silicate 4 per cent (pulp basis), hydrogen peroxide 2 and 4 per cent (pulp basis). When 2 per cent hydrogen peroxide was used the bleaching times were 1 and 30 h, and with 4 per cent hydrogen peroxide the time was 30 h. The following conditions were used for second stage bleaching with sodium borohydride: pulp consistency 30 per cent; sodium borohydride 1 per cent (pulp basis); sodium hydroxide 1 per cent (pulp basis); bleaching time 1.5 h. The conditions for third stage hydrogen peroxide bleaching were as follows: pulp consistency 30 per cent; sodium silicate 2 per cent (pulp basis); hydrogen peroxide 2 per cent (pulp basis); bleaching time 18 h. At the end of the bleaching sequence the pulp was washed, suspended in dilute acid solution (pH 4 with H_2SO_4), collected and washed again with purified water.

Handsheets

Handsheets of 60 g/m^2 were prepared with recirculation of white water to minimize the loss of fines.

Brightness Measurements

The brightness of handsheets was measured at a wavelength of 457 nm with an Elrepho reflectometer calibrated on the basis of MgO=100.

Irradiation of Handsheets

Handsheets were irradiated in a Q.U.V. Accelerated Weathering Tester (manufactured by the Q-Panel Company, Cleveland, Ohio, U.S.A.) which contained eight fluorescent FS 40 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

A Spectra-Tech Diffuse Reflectance Accessory was used with a Mattson Alpha Centauri FTIR spectrometer equipped with a water-cooled source, a computer-controlled iris and a DTGS detector. The spectra were obtained by reflecting the radiation off the rougher (wire) side of 14 mm square samples of the handsheets and were ratioed to a background spectrum, collected at the same instrumental settings, of finely powdered potassium bromide. Both the diffuse and specular components were obtained. The reflectance spectra were collected at a resolution of 4 cm^{-1} and are averages of 128 scans (measurement time of 5 minutes). They were converted to Kubelka-Munk units so that the band heights would be approximately linear with concentration. The spectral baselines were corrected using the instrument software by assuming that the baseline was zero at 3850, 2550, 1850, 760 and 475 cm^{-1}. Interference by water vapour bands arising from incomplete compensation was reduced by using a 7-point smoothing routine.[5] Overlapping of the spectra was done with the instrumental software and frequencies were obtained by using the "read cursor" facility.

RESULTS AND DISCUSSION

Brightness and reversion

The *E. regnans* cold soda pulp was bleached in a single stage with different amounts of hydrogen peroxide and also in 2- and 3-stage sequences which incorporated sodium borohydride as a second stage treatment. Bleaching was done at high consistency, low temperature with long reaction times because the conditions were found to be the best way of bleaching the pulps to a very high brightness level. The brightness levels of the unbleached pulp and various bleached pulps are given in Table 1. The use of 4 per cent hydrogen peroxide gave very high brightness pulps, and additional treatment with sodium borohydride and hydrogen peroxide did not appreciably increase the brightness level. The bleached pulp was treated with sodium borohydride to determine whether the use of a small amount of this reducing agent would lessen the brightness reversion caused by exposure to light.

The brightness levels of the pulps after irradiation with light for various periods are listed in Table 1. The pulps bleached to a high brightness with only hydrogen peroxide were affected to the greatest extent. A second stage treatment with sodium borohydride resulted in a greater brightness stability even when it was followed with a further hydrogen peroxide bleaching stage.

Infrared spectroscopic studies

The FTIR spectra of handsheets of the pulps before and after irradiation have been measured to obtain information about the chemical changes causing the changes in brightness. The method used has the advantage that the possibilities for introducing artifacts during sample preparation are avoided and there is no interference in the important region near 1640 cm^{-1} by water introduced with the alkali halide medium as in transmission spectra. The wire side was used because it scatters radiation more diffusely than does the mirror-plate side. The random ordering of the fibres in the surfaces of the sheets and the uniform roughnesses of the surfaces are important to the maintenance of the uniformity of scattering necessary for semiquantitative measurements. The spectra obtained in reflection have been linearized by using the Kubelka-Munk transformation which has previously been employed in the UV and visible regions of the reflectance spectra

TABLE 1

Brightness Levels of Handsheets Before and After Irradiation

Irradiation time (min)	Pulps used to prepare handsheets					
	Unbleached	2% H_2O_2 (1 h)	2% H_2O_2 (30 h)	4% H_2O_2 (30h)	4% H_2O_2/ $NaBH_4$	4% H_2O_2/$NaBH_4$/ 2% H_2O_2
0	56.0	74.5	84.2	87.2	87.7	88.4
15	-	-	-	73.1	77.1	77.6
30	-	64.5	70.9	69.1	74.1	75.4
60	50.8	60.8	65.0	64.1	70.5	71.7
120	47.7	56.2	56.8	59.9	65.5	66.4
240	43.8*	51.5	52.4	53.4*	58.0*	60.0*
360	-	48.1*	48.2*	-	-	-

* Sample used for infrared spectrum

of papers.[6] The maximum values of the Kubelka-Munk function observed in the part of the spectrum (1560-1800 cm^{-1}) of most interest was about 0.6 which is within the region where the linearity of the function with the concentration of the absorbing species is expected to be good. The main chromogene groups in lignin and in the other aromatic components of wood related to lignin absorb in this region.[3] In those parts of the spectrum containing more strongly absorbing vibrations, such as near 3400 and 1000 cm^{-1}, the linearity of the Kubelka-Munk function with concentration of absorbing species breaks down and this means of direct study of the surface is not applicable.

Figure 1 is a plot of the Kubelka-Munk (K-M) function versus frequency for the unbleached pulp and pulps bleached in one, two and three stage bleaching procedures. In comparing our results in this part of the spectrum with those of other workers[2-4] it should be remembered that their pulping did not involve alkali so that the pulps retained much of their initial content of carboxyl and ester groups. These groups, which absorb near 1740 cm^{-1}, are present in our unbleached pulp in only very low concentrations. It is clear that the overall effect of the bleaching treatments on the spectrum of our pulp has been to progressively reduce absorption in the region 1620-1700 cm^{-1} and to increase absorption in the region 1700-1780 cm^{-1} while leaving the region 1560-1620 cm^{-1} little changed. The bands in this last region are shown as they were observed and have not been normalized. The near constancy of the band near 1600 cm^{-1} which arises from a C = C vibration in the aromatic ring indicates that the aromatic lignin skeleton was altered to only a minor extent by the bleaching treatment and that reaction was limited mainly to the side chains. The most marked reduction in intensity in the 1620-1700 cm^{-1} region followed the initial treatment with 4% hydrogen peroxide and the next the subsequent treatment with sodium borohydride. The decrease following the hydrogen peroxide treatment would be expected if the functional groups absorbing in this region contribute to lack of brightness since this treatment gave the greatest increase in brightness. The

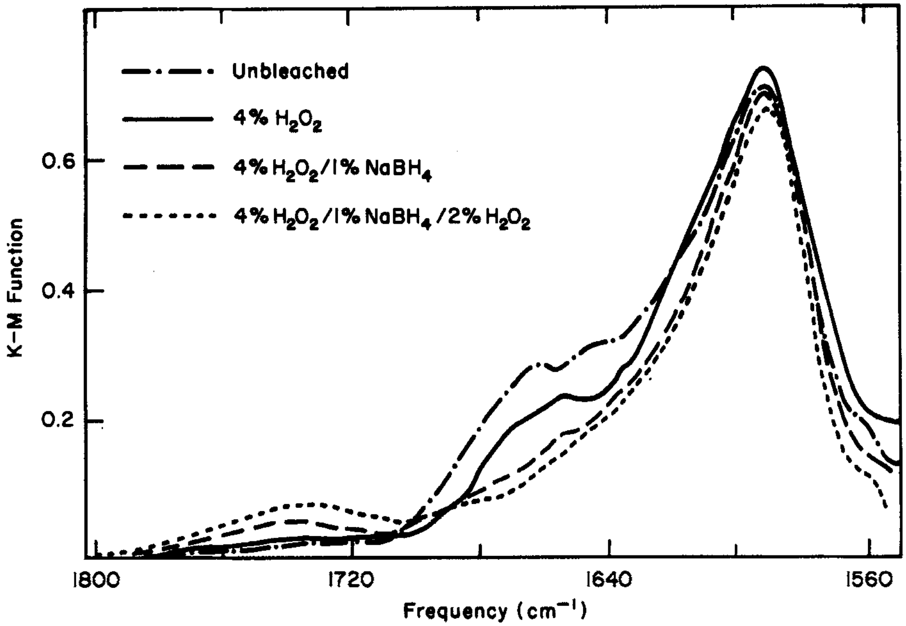

FIGURE 1. DRIFT Spectra (1560-1800 cm^{-1}) of sheets made from unbleached pulps and from pulps bleached by various procedures.

reduction following the borohydride treatment, on this basis, would have been expected to be less. The spectrum of the unbleached sheet shows two peaks near 1660 and 1640 cm^{-1}. The higher frequency peak could arise from unsaturated ketones, particularly aromatic ketones, and the lower frequency peaks from quinones, or keto groups conjugated to more than one aromatic ring. The main difference is that the lower frequency band arises from a more strongly conjugated group. Another possible contributor to absorption in this region (ca 1640 cm^{-1}) is a vibration of water absorbed on the pulp. However, since the spectra were obtained under constant temperature and humidity conditions, variations from this source are expected to be only small.

Each stage of the bleaching treatment resulted in increased intensity in the region 1700-1780 cm^{-1}. Bands in this region arise from vibrations of non-conjugated carbonyl groups such as those in carboxylic acids and esters. This result is not surprising in the case of alkaline hydrogen peroxide treated pulp since it is known that alkaline peroxide depolymerizes cellulose and oxidizes reducing end groups to glycosido-arabonic acids.[7] It has been found that about 60 per cent of the hydrogen peroxide used to bleach Eastern spruce groundwood was consumed by the carbohydrate fraction of the pulp.[8] Moreover, it has been suggested[9] that alkaline peroxide can create carbonyl groups when reacting with lignin. What is surprising, however, is that the greatest increase in intensity in this region appeared to follow treatment with sodium borohydride which is expected to reduce carbonyl groups rather than create them. However, it has been suggested[4] that the alkalinity involved in bleaching with borohydride can create new functional groups from substituents indifferent towards reduction. Overall, though, since the brightness increases despite the increase in absorption in this part of the spectrum these functional groups must be lesser contributors of colour than those which absorb at the lower frequencies.

The DRIFT spectra of the previously discussed unbleached and bleached pulps after UV exposure for 4 h are shown in Figure 2. Before comparing them we need to note that yellowing is mainly a surface phenomenon[10] and falls off in intensity at greater depths. In theory[11], this would seem to invalidate the use of the Kubelka-Munk transformation, but in practice, the close correspondences in intensities between the 1592 cm^{-1} bands in each pair of spectra of control and irradiated sheets suggest that the relationship between the amount of absorbing species and the band intensity still pertains. This would be so if the intensity of yellowing is relatively uniform within the depth of penetration of the diffuse infrared radiation. The spectra of the 2- and 3-stage bleached pulps were almost identical after irradiation and this is

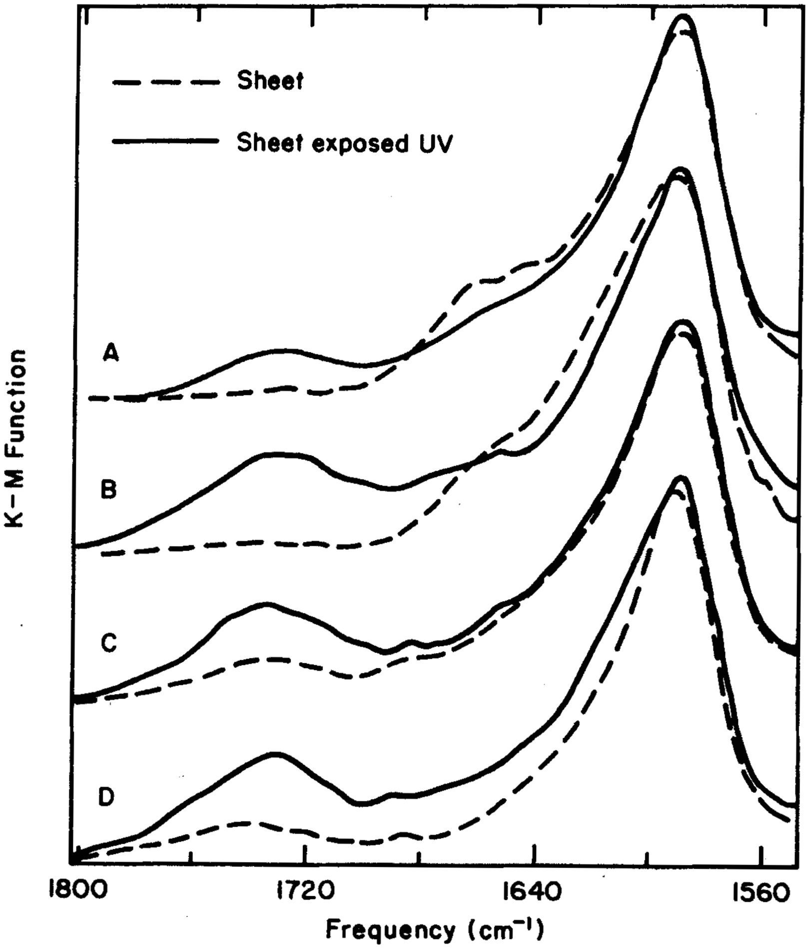

FIGURE 2. DRIFT Spectra (1560-1800 cm^{-1}) of sheets before and after exposure to UV for 4 h. A. Unbleached pulp. B. Pulp bleached by 4% H_2O_2. C. Pulp bleached by 4% H_2O_2/1% $NaBH_4$. D. Pulp bleached by 4% H_2O_2/1% $NaBH_4$/2% H_2O_2.

consistent with their level of brightness (58 and 60, respectively). The main differences in the spectra of the irradiated pulps were comparable to those observed for the un-irradiated pulps, namely, the more highly bleached pulps had more intense bands in the region 1700-1760 cm^{-1} and a reduced width of the high frequency side of the 1592 cm^{-1} band. However, in the region 1620-1700 cm^{-1} the spectra of the various pulps were affected in different ways by irradiation. With the unbleached pulp the absorption appears to have been reduced whereas with the pulp bleached in three stages the absorption increased. There was a very small increase in absorption with the pulp bleached in two stages whereas the hydrogen peroxide bleached pulp had a lower absorption in the lower frequency half of this region but a higher absorption in the other portion. The apparent reduction in absorption following UV irradiation of the unbleached pulp is anomalous if bands in this region are indicative of the presence of chromophores, since the UV irradiated sheet has lower brightness. There is no obvious explanation but, perhaps, some changes in the underlying broad band near 1640 cm^{-1} may arise from the presence of water in the pulp.

The nature of the groups absorbing in the region 1560-1800 cm^{-1} was further investigated by measurement of the spectra of bleached and UV exposed sheets after exposure to ammonia vapour for 2.5 h. The results are shown in Figure 3. The exposure to ammonia produced only a small reduction in intensity in the region 1720-1760 cm^{-1} of the highly bleached pulp but a very considerable reduction in the spectrum of the UV-exposed highly bleached pulp. The latter sheet was visibly darkened. The expected effect of exposure to ammonia is to convert carboxyl groups to salt groups and shift the C = 0 stretching frequency from a single band near 1740 cm^{-1} to two bands in a lower frequency region of the spectrum.[12] Thus it would appear that the bleaching treatment has produced a small number of carboxyl groups in the pulp but that the UV treatment has produced many more.

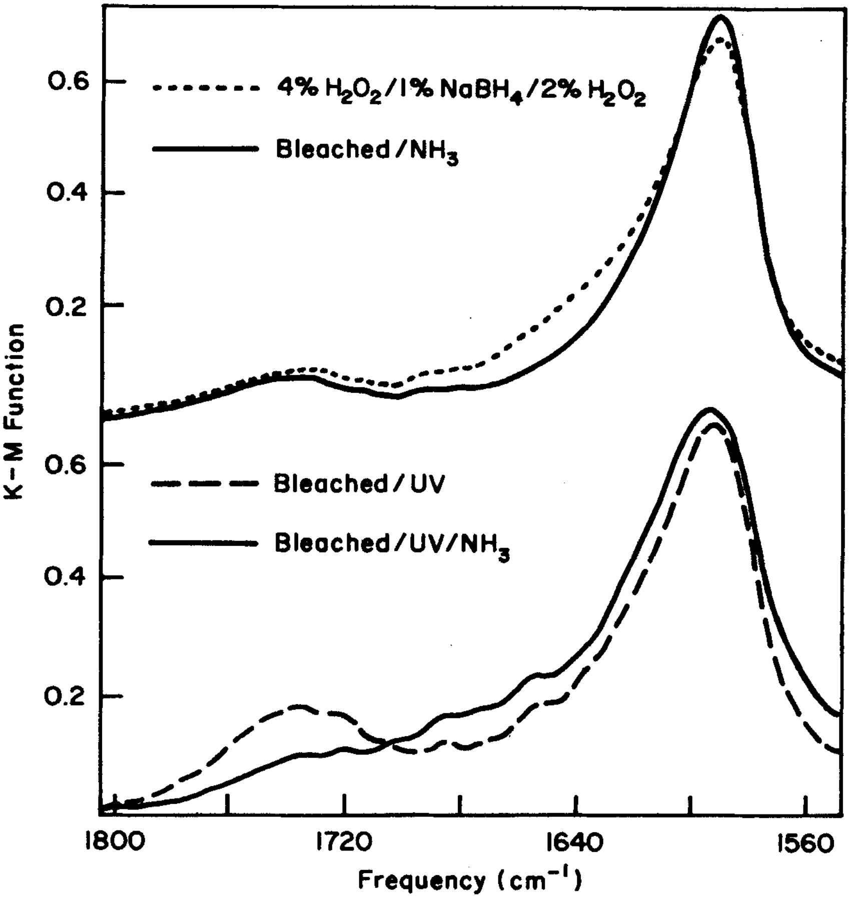

FIGURE 3. DRIFT Spectra (1560-1800 cm^{-1}) of sheets from pulps bleached by 4% H_2O_2/1% $NaBH_4$/2% H_2O_2. Control sheets, sheets exposed to NH_3 for 2.5 h, sheets exposed to UV for 4 h, and to UV for 4 h and NH_3 for 2.5 h.

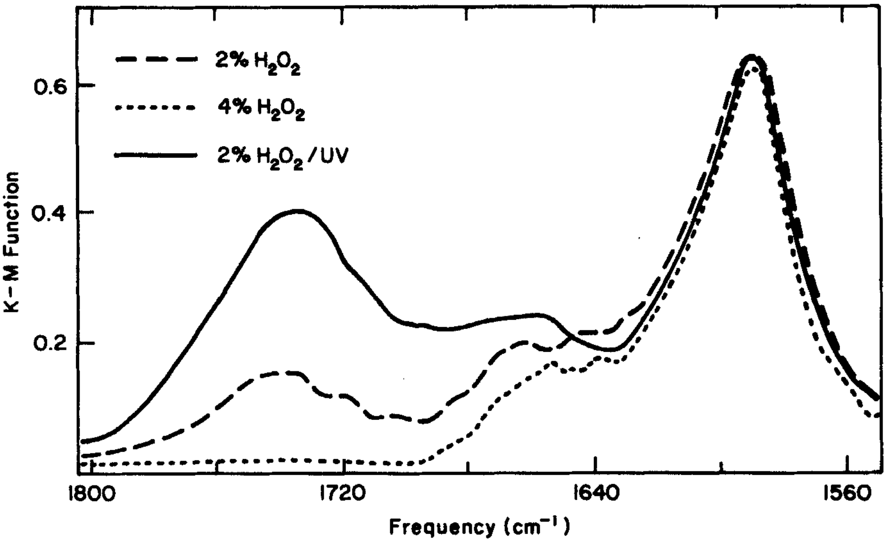

FIGURE 4. DRIFT Spectra (1560-1800 cm^{-1}) of sheets from pulps bleached by 2% H_2O_2 for 1 h, by 4% H_2O_2 for 1 h, by 2% H_2O_2 for 1 h and made into sheets, before exposure to UV for 6 h.

The spectra of a sheet made from pulp bleached with 2% hydrogen peroxide for 1 h and of a sheet made from the same pulp and then exposed to UV for 6 h are shown in Figure 4 with that of a sheet made from pulp bleached with 4% hydrogen peroxide for 30 h. Not surprisingly, the sheet bleached to the lower brightness shows more absorption in the region 1620-1680 cm^{-1} than does the sheet bleached to higher brightness. However, it also shows greater absorption in the 1700-1780 cm^{-1} region despite having been exposed to lower levels of hydrogen peroxide. This could be explained if alkaline peroxide had the ability to remove carbonyl groups as well as create them[9] and if the lower level of peroxide used here was insufficient to accomplish the removal. After exposure to UV light for 6 h the sheet showed much more absorption in the higher

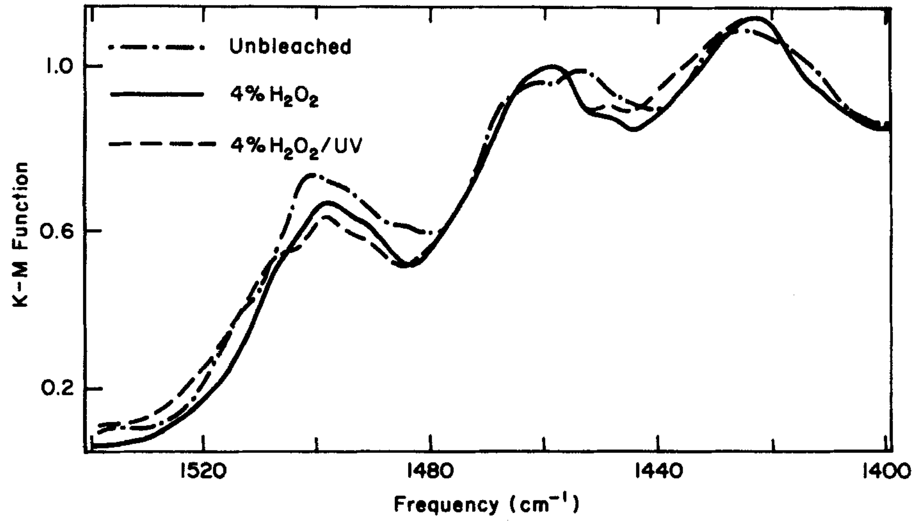

FIGURE 5. DRIFT Spectra (1400-1520cm^{-1}) of sheets from unbleached pulp, from a pulp bleached by 4% H_2O_2 and a pulp exposed to UV for 4 h after bleaching.

frequency region as well as some increase in absorption near 1660 cm^{-1}. There appear to be two bands in the higher frequency region near 1720 and 1740 cm^{-1}. Similar bands were observed by Hon and Chang[13] following prolonged UV irradiation of southern yellow pine wood and of purified wood cellulose. They assigned the bands to saturated carbonyl and carboxyl groups, respectively.

Changes resulting from bleaching and exposure to UV irradiation might also be expected in other regions of the spectra of the sheets. The next part of the spectrum examined was from 1250-1540 cm^{-1}. However in Figure 5 only the part of the spectrum from 1400-1540 cm^{-1} is reproduced since the various spectra showed little change in the region 1250-1400 cm^{-1}. Figure 5 shows that the spectrum of a sheet bleached with 4% hydrogen peroxide differs from that of an unbleached sheet. The spectra of sheets from the two multistage bleaching sequences are not shown because they are almost superimposable on the spectrum of the sheet bleached with 4% hydrogen peroxide. The differences between the spectra in Figure 5 have been confirmed by studies of second derivative spectra in the same region.[14] Such spectra are much sharper and the band resolution is much improved. Thus there are differences in intensities for components of each of the three major band envelopes, with the lower intensity of the 1452 cm^{-1} band in the spectrum of the bleached sheet being most marked. The only changes to the spectrum in this region following exposure of the bleached sheet to UV light were the appearance of a shoulder at 1505 cm^{-1} and a little more intensity around 1450 cm^{-1}.

In general, bands in the 1400-1540 cm^{-1} region of the spectra of lignocelluloses arise from aromatic skeletal vibrations in lignin and from C-H deformation vibrations of lignin and of polysaccharides.[15] More precise assignments are difficult because, hitherto, all of the major bands have been assigned as single peaks. Figure 5 shows clearly that they are not. Of particular interest is the assignment of the C-H bending vibration in methyl groups since a decrease in methoxyl content has been linked with the yellowing of wood exposed to UV light.[16] Originally, 1470 cm^{-1} was the frequency ascribed to absorptions of this vibration[17] but it has since been noted[15] in model compound spectra that bands at this frequency possess a doublet structure. Moreover, since the original analysis of methoxyl content relied on production of methyl iodide, any change in the methoxyl group which no longer led to this product would have appeared to be demethoxylation. Another band associated with vibrations of methoxyl groups is that near 2840 cm^{-1} which appeared only as a shoulder in our spectra. There was no evidence of any marked loss of intensity of this band in any of the spectra of the bleached or UV exposed sheets. It appeared that bleaching with 4% hydrogen peroxide produced changes in all the bands in the region 1400-1540 cm^{-1}. At least two of the bands are derived from aromatic skeletal modes and thus are possibly part of the chromogenic system. Changes in the other bands might also be involved in changes in colour in so far as they relate to the introduction or removal of auxochromic groups.[3] More background work is needed to provide a more precise interpretation of the nature and behaviour of these bands.

Bands in other parts of the spectra such as in the O-H and C-O stretching regions (3100-3700 cm^{-1}) and 1000-1200 cm^{-1} are also likely to be affected by the bleaching treatments and exposure to UV light. However, absorption in these parts is so intense as to be in the non-linear region of the plot of K-M function versus concentration. These parts of the spectrum need to be studied by using dilution techniques.

CONCLUSIONS

E. regnans cold soda pulp can be bleached with 4 per cent hydrogen peroxide in a single stage to very high brightness which is only slightly increased by additional treatment with sodium borohydride and hydrogen peroxide. Brightness was decreased by exposure to UV light with the effect being greatest for the brightest pulps bleached solely with hydrogen peroxide. Greater brightness stability was shown by pulps given a second stage treatment with sodium borohydride.

The infrared spectra of the wire side of the sheets were measured by the DRIFT method and used to follow chemical changes in the pulps resulting from the bleaching treatments and from exposure of the treated pulps to UV light. The resultant yellowing must have caused the sheets to become optically heterogeneous, but the fact that the intensities of the 1592 cm^{-1} bands in the spectra of corresponding control and UV-exposed sheets were almost the same suggested that the relationship between the band intensities and concentrations of chromophores had not been badly disturbed. The dominant feature of the spectra was the increase of intensity of bands in the region 1700-1760 cm^{-1} which was attributed to oxidation of the lignocellulose by the oxidative treatments and by UV light. This is probably unrelated to the colour since the intensity of the bands increased with both treatments, whereas pulp brightness was markedly reduced by exposure to UV light. However, in most cases a reduction in intensity of bands in the region 1620-1700 cm^{-1} was found to accompany increases in brightness. Nonetheless, changes in the spectra and in the chemistry accompanying the studied bleaching sequence and subsequent UV exposure are very complex and some features need further explanation.

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