Light-Induced Bleaching of High-Yield Pulps Part I. Sensitized Bleaching of Pulp Sheets

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LIGHT-INDUCED BLEACHING OF HIGH-YIELD PULPS
PART I. SENSITIZED BLEACHING OF PULP SHEETS[1]

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ABSTRACT

Bleached high-yield pulps undergo a much higher rate of light-induced brightness reversion than their chemical counterparts. This tendency to discolor is one of the main factors limiting the application of high-yield pulps to short-term products such as newsprint, tissue, toweling, and foodboard.

The present study was conducted to determine whether the light absorption responsible for aging could be utilized to activate and subsequently destroy the chromophores in high-yield pulps. This would permit production of a bleached pulp.

Aspen thermomechanical pulp (TMP) and white oak chemimechanical pulp (CMP) sheets were bleached by irradiation with near ultraviolet light (300-400 nm) while saturated with alcohols in the presence of oxygen. Addition of benzophenone and/or hydrogen peroxide as photosensitizers to the alcohols prior to irradiation accelerated the bleaching rates and increased the sheet reflectance (457 nm) 20 to 30 points. High light intensity enhanced bleaching; alkali and water retarded the brightening process.

Benzophenone and hydrogen peroxide accelerate bleaching, presumably by utilizing light energy to synthesize significant amounts of organic peroxides (α-hydroxyhydroperoxides) for light-induced bleaching. It is suggested that in the absence of added benzophenone or hydrogen peroxide, chemical groups in lignin (i.e., α-carbonyl groups) are responsible for sensitizing the formation of adequate quantities of these peroxides for bleaching to occur. The light also accelerates bleaching, possibly by activating lignin chromophores, and this enhances their reactivities towards the alcohol peroxides.
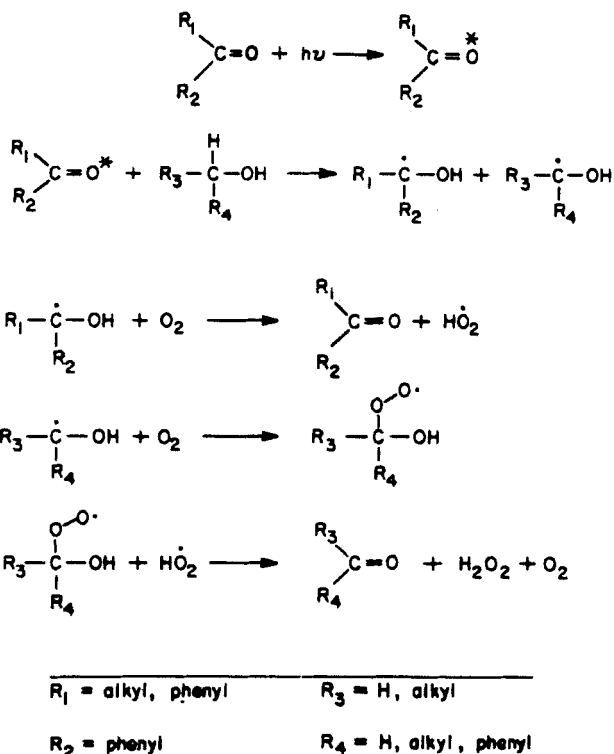
INTRODUCTION

High-yield pulps bleached by alkaline peroxide oxidation undergo

rapid brightness reversion when exposed to air in daylight. The

bleached pulp still contains chemical groups that absorb ultraviolet (UV) light with wavelength greater than 290 nm, because sunlight at the earth's surface contains practically no energy distribution below this wavelength. Leary[3] postulated and Lin and Kringstad[4-8] and Imsgard, Falkehag and Kringstad[9] elucidated the mechanism of this discoloration and showed that UV light (300-400 nm) induced the formation of quinones in isolated lignin and lignin model compounds. In high-yield pulps these quinones absorb light in the blue-green region and, therefore, make the pulps appear yellow. This light aging is mainly responsible for limiting commercial application of high-yield pulps.

Hypothetically, if the wavelength of the light responsible for light-induced brightness reversion (light-aging) were utilized to bleach the chromophores in high-yield pulps by photooxidation, a product with improved brightness stability should be obtained because the chromophores absorbing light in that region (300-400 nm) would be destroyed.

Irradiation of carbonyl-containing sensitizers or hydrogen peroxide in alcohols in the presence of oxygen converts the alcohols into α-hydroxyhydroperoxides and organic acids.[10-12] The α-hydroxyhydroperoxides are reactive oxidizing agents. They also decompose to form carbonyl compounds and hydrogen peroxide. The ketyl radicals formed after the carbonyl-containing sensitizers abstract hydrogen atoms can react with molecular oxygen thereby regenerating the sensitizers and forming additional quantities of hydrogen peroxide. These reactions are shown in scheme 1. Some specific photooxidations of alcohols by hydrogen peroxide[13] and some carbonyl-containing sensitizers such as benzophenone,[14-16] benzoquinone,[17] and anthraquinone derivatives[18] have been reported. More recently, Brunow and Eriksson[19] showed that 4-hydroxy-3-methoxyacetophenone sensitized the complete destruction of 1-(4-hydroxy-3-methoxyphenyl)-propanol when these compounds were irradiated together in ethanol in the presence of oxygen. The authors did not consider the role of the alcohol solvent, but their results demonstrated the efficient and selective oxidizing potential of photooxidation in alcohols and oxygen for a lignin model.

$$\begin{array}{c} R_1 \\ \diagdown \\ R_2 \end{array} C{=}O \; + \; h\nu \; \longrightarrow \; \begin{array}{c} R_1 \\ \diagdown \\ R_2 \end{array} C{=}\overset{*}{O}$$

$$\begin{array}{c} R_1 \\ \diagdown \\ R_2 \end{array} C{=}\overset{*}{O} \; + \; R_3{-}\overset{\overset{H}{\displaystyle|}}{\underset{\underset{R_4}{\displaystyle|}}{C}}{-}OH \; \longrightarrow \; R_1{-}\overset{\cdot}{\underset{\underset{R_2}{\displaystyle|}}{C}}{-}OH \; + \; R_3{-}\overset{\cdot}{\underset{\underset{R_4}{\displaystyle|}}{C}}{-}OH$$

$$R_1{-}\overset{\cdot}{\underset{\underset{R_2}{\displaystyle|}}{C}}{-}OH \; + \; O_2 \; \longrightarrow \; \begin{array}{c} R_1 \\ \diagdown \\ R_2 \end{array} C{=}O \; + \; H\overset{\cdot}{O}_2$$

$$R_3{-}\overset{\cdot}{\underset{\underset{R_4}{\displaystyle|}}{C}}{-}OH \; + \; O_2 \; \longrightarrow \; R_3{-}\overset{O{-}O\cdot}{\underset{\underset{R_4}{\displaystyle|}}{C}}{-}OH$$

$$R_3{-}\overset{O{-}O\cdot}{\underset{\underset{R_4}{\displaystyle|}}{C}}{-}OH \; + \; H\overset{\cdot}{O}_2 \; \longrightarrow \; \begin{array}{c} R_3 \\ \diagdown \\ R_4 \end{array} C{=}O \; + \; H_2O_2 \; + \; O_2$$

R_1 = alkyl, phenyl	R_3 = H, alkyl
R_2 = phenyl	R_4 = H, alkyl, phenyl

ML85 5357

SCHEME 1. Reactions of carbonyl-containing sensitizers in alcohols in the presence of UV light and oxygen. (ML85 5357)

In our preliminary work, aspen thermomechanical pulp (TMP) and white oak chemimechanical pulp (CMP) sheets were irradiated with UV light (300-400 nm) while steeped in alcohols in the presence of oxygen. Substantial bleaching occurred compared to similar irradiation in the absence of alcohols or oxygen. The purpose of this investigation was to study the light-induced bleaching associated with the photooxidation occurring when the alcohol-saturated pulp sheets were irradiated in the presence of oxygen. This paper describes the light-induced bleaching of aspen TMP and white oak CMP sheets, including the effects of the various bleaching parameters. Part II emphasizes the light-induced bleaching of these and other

pulps in slurry form and discusses the effect of the bleaching con-
ditions on the strength and optical properties of the bleached pulps.

RESULTS AND DISCUSSION

Light-Induced Bleaching

The reflectance (457 nm) of aspen TMP sheets increased signi-
ficantly when they were irradiated with UV light (300-400 nm) while
steeped in some common alcohols in the presence of oxygen (Table 1).
For the homologous series of straight chain alcohols, the bleaching
effect lessened appreciably as the carbon chain length of the
alcohols increased beyond four carbon atoms. For bleaching to
occur, the alcohols must physically saturate (wet) the pulp figers;
part of the decrease in bleaching was therefore attributed to the
increasing hydrophobic character of the alcohols as the carbon chain
length increased. Although complete data are not available, heat-
of-wetting studies have shown that methanol wets wood fibers three-
fourths as well as does water,[20] with the fiber-wetting abilities
decreasing as the carbon chain length of the alcohols increased.
Each of the alcohols that gave significant bleaching during irradia-
tion wets the pulp well. However, wetting the pulp is not the only
necessary condition. The alcohols must also be good hydrogen donors
for bleaching to occur.

Alcohols are transparent to near UV light. But when they are
irradiated in the presence of sensitizers (including photosensitive
groups in lignin) and oxygen, they undergo photooxidation forming
alcohol peroxides (i.e., α-hydroxyhydroperoxides).[21] Sensitized
photooxidation of methanol, for example, gave on analysis a peroxide
mixture that was 58% hydrogen peroxide and 42% organic peroxide.
The organic peroxide was thought to consist of hydroxymethylhydro-
peroxide and di(hydroxymethyl)hydroperoxide. Thus the light-induced
bleaching in the oxygenated alcohols was attributed to the reaction(s)
of alcohol peroxides with lignin chromophores in the pulp sheets.
The ratio of the hydrogen peroxide as determined by the titanium (IV)
method to the total peroxides as hydrogen peroxide found iodometrically
(Table 1) provides an indication of the relative stabilities of the

TABLE 1

Effect of Some Common Alcohols on the Sensitized and Unsensitized Light-Induced Bleaching of Aspen TMP Sheets (Irradiated 24 h at 45°C; Benzophenone/Pulp = 6%; Liquor/Pulp (g/g) = 12.2)

Solvent	Wood wetting ability relative to H_2O (Ref. 20)	H_2O_2 from alcohol	Total peroxide from alcohol (as H_2O_2)[1]	Ratio of H_2O_2 to total peroxides	Handsheet reflectance[2] %	
					Unsensitized	Sensitized
		— — Micromoles — —				
Control	--	--	--	--	53	--
Methanol	0.75	206	235	0.88	66	73
Ethanol	0.63	352	432	0.81	63	73
n-Propanol	0.33	265	317	0.84	62	68
Isopropanol	--	470	470	1.00	60	72
n-Butanol	0.12	132	279	0.47	60	63
n-Hexanol	--	109	--	--	54	--
n-Octanol	--	82	--	--	43	--
Allyl alcohol	--	173	270	0.64	73	76
Benzyl alcohol	--	32	91	0.35	73	73
Methyl cellosolve	--	44	97	0.45	76	76

[1]H_2O_2 and total peroxides were generated by irradiating 2 ml of neat solvent containing 8 mg benzophenone 12 h without pulp sheet present.
[2]Sheets bleached by irradiating 24 h.
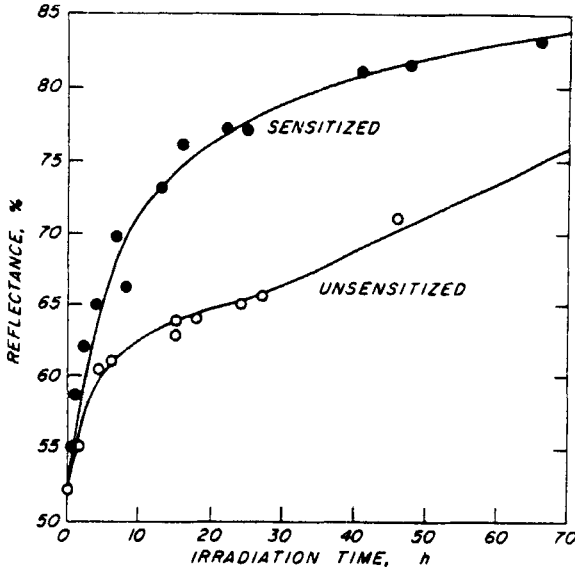
M 149 434

FIGURE 1. Light-induced bleaching of aspen TMP sheets in MeOH
with and without benzophenone (BP) (irradiated at 45°C;
BP/pulp = 3%; liquor/pulp (g/g) = 12.2). (M149 434)

various alcohol peroxides because the hydrogen peroxide arises from
decomposition of the organic hydroperoxide. The lower this ratio the
more stable the alcohol peroxide. For example, methyl cellosolve,
allyl alcohol, and benzyl alcohol have relatively low ratios of
titanium (IV) hydrogen peroxide to iodometric total peroxides.

     Because aspen TMP sheets bleached almost as well in methanol
as in methyl cellosolve, allyl alcohol, and benzyl alcohol when
benzophenone was added prior to irradiation, methanol was used
exclusively to study the light-induced bleaching variables. Methanol
should also serve as a model for the homologous series of primary
alcohols.

     The light-induced bleaching rates for aspen TMP and white oak
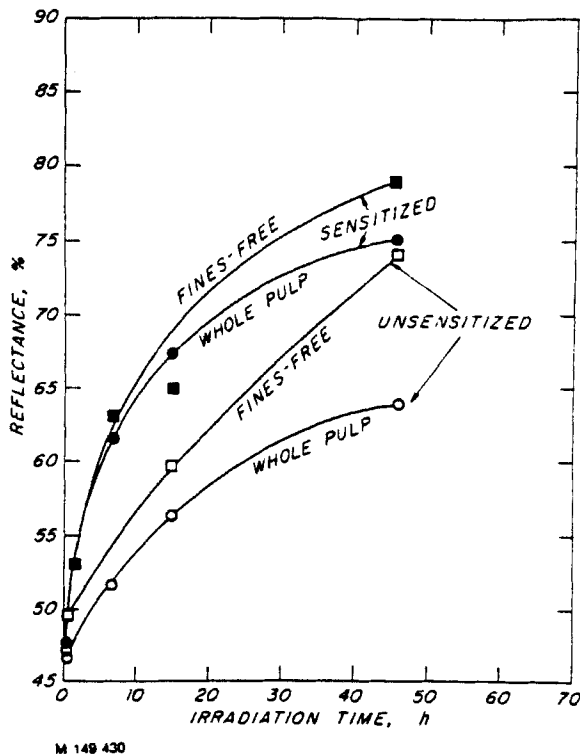CMP (whole and fines-free) sheets are given in Figures 1 and 2.

FIGURE 2. Light-induced bleaching of white oak CMP sheets in MeOH with and without benzophenone (BP) (irradiated at 45°C; BP/pulp = 3%; liquor/pulp (g/g) = 12.2). (M149 430)

The bleaching rates were accelerated by the addition of benzophenone prior to irradiation. This enhanced bleaching in the presence of sensitizer was attributed to the significant buildup and consumption of peroxides in the bleaching liquors during irradiation (Figure 3). There was very little formation of peroxides in the absence of sensitizer.

In contrast to aspen TMP, white oak CMP contains about 30% fines. The minus 200 mesh pulp fraction represents the fines which consist mostly of flakes from the middle lamella, short ray cells,
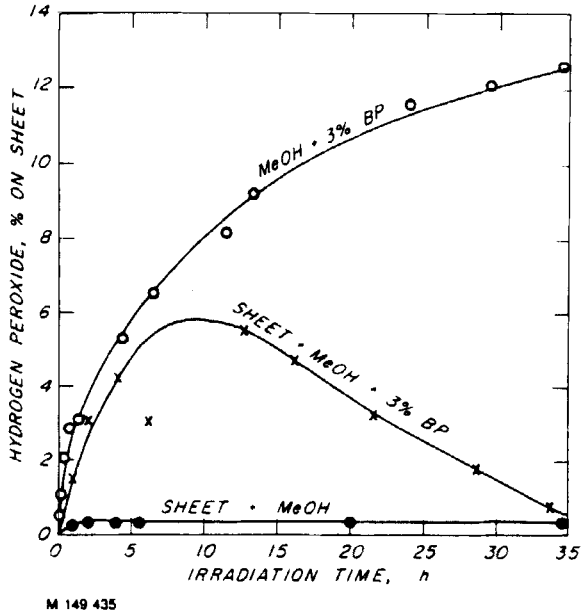
M 149 435

FIGURE 3. Light-induced peroxide production and consumption
during light-induced bleaching of aspen TMP sheets in MeOH
with and without benzophenone (BP) (irradiated at 45°C;
BP/pulp = 3%; liquor/pulp (g/g) = 12.2). (M149 435)

and ribbons from the fiber wall. The fines greatly affect the
optical properties as they contain additional lignin and resins.
Thus a pulp with a high fines content is more difficult to bleach
than one low in fines.

    Some white oak CMP was fractionated into a fines-free fraction
which was made into sheets. The whole and fines-free white oak CMP
sheets gave two distinct bleaching rates when they were irradiated
while saturated with methanol in the presence of oxygen (Figure 2).
Removing the fines from the white oak CMP gave a more photobleachable
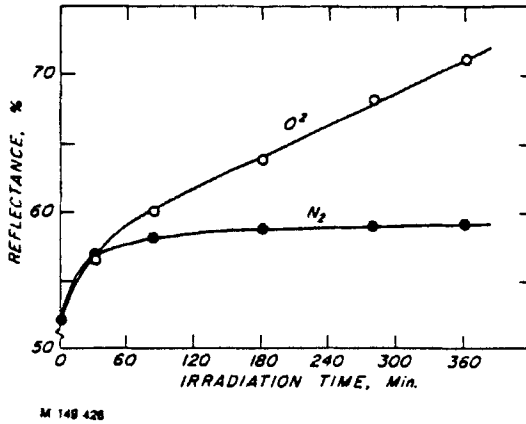sheet.

M 149 426

FIGURE 4. Effect of oxygen versus nitrogen on the light-induced bleaching of aspen TMP sheets in MeOH sensitized with benzophenone (BP) (irradiated at 45°C; BP/pulp = 2.5%; liquor/pulp (g/g) = 12.2). (M149 426)

Aspen TMP sheets bleached at a faster rate when irradiated while steeped in methanol solutions of benzophenone in oxygen than in nitrogen (Figure 4). The fast initial bleaching in nitrogen was attributed to autooxidation involving absorbed oxygen entrapped in fiber capillaries and void spaces. A hydrogen peroxide analysis of the spent methanol by the titanium (IV) method after bleaching was completed, revealed only 1% hydrogen peroxide in nitrogen compared to 7% in oxygen. Thus oxygen was important for the production of organic peroxides that appear to be responsible for the bleaching.

Preliminary experiments comparing the accelerated light-induced brightness reversion of pulp sheets bleached with light with pulps bleached by alkaline peroxide indicate that the light-bleached pulps are more stable. The complete results will be treated in Part II of this paper.

Effect of Bleaching Variables

Sensitizers.--As already discussed, benzophenone when added to the methanol prior to irradiation has an accelerating effect on the

bleaching rates of aspen TMP and white oak CMP (whole and fines-free) sheets (Figures 1 and 2). However, the efficient sensitizing of benzophenone was considerably lessened after 40 h of irradiation as the peroxides decreased to a low level (Figure 3). Gas chromatographic/mass spectrometric analysis of the benzophenone-methanol solutions after 91 h irradiation (Table 2) indicated that benzophenone was converted into benzoic acid and 1,1-diphenylglycol. The yield of these products was estimated to be 4% and 45%, respectively, based on the area percentages of these components in the gas chromatogram.

Natural sensitizers in the pulp sheet (i.e., α-carbonyl groups in lignin) initiate the photooxidation of alcohols also. These natural sensitizers account for the "unsensitized" bleaching rates for aspen TMP and white oak CMP sheets when they were irradiated while steeped in methanol in the presence of oxygen (Figures 1 and 2). Even in this case, bleaching was ascribed to the low levels of methanol peroxide and hydrogen peroxide generated simultaneously with the light activation of the lignin.

Hydrogen peroxide also enhanced the bleaching of aspen TMP sheets when added to methanol prior to irradiation (Figure 5). The increased bleaching upon irradiation when hydrogen peroxide was added was considerably greater than the bleaching obtained with hydrogen peroxide in the dark. This increased bleaching was attributed also to the methanol peroxide formed when hydrogen peroxide reacted with methanol. In this case, the light activated the lignin chromophores and/or the methanol peroxide thereby accelerating the bleaching. The upper curve in Figure 5 shows the bleaching effect of methanol peroxide and hydrogen peroxide with light activation of the lignin chromophores; the lower curve shows the bleaching effect of methanol peroxide and hydrogen peroxide in the dark. The difference between the upper and lower curves represents the light-induced bleaching effect.

Water.--When aspen TMP sheets were irradiated while saturated in methanol-hydrogen peroxide and methanol-benzophenone solutions

TABLE 2

Gas Chromatographic/Mass Sspectrometric Analysis of Benzophenone-Methanol Solutions (100 mg Benzophenone Dissolved in 5 ml Methanol; Irradiated 91 h at 35°C)

| Compound name (Gas chromatography retention time)	Ionization				Structural assignment
	Electron		Chemical		
			Iso-butane	Ammonia	
	m/e	R.A.[1]	- - m/e - -		
Benzoic acid (1.20)	51	9.6			
	77	69.9			
	105	100.0			
	122	76.3			
Benzophenone (9.05)	51	20.4	183		$[(C_6H_5)_2\text{-C=O+H}^+]^+$
	77	57.8			
	105	100		200	$[(C_6H_5)_2\text{-C=O+NH}_4^+]^+$
	182	57.2			
1,1-Diphenyl-glycol (22.75)	51	1.8	197		OH OH $[(C_6H_5)_2\text{-C-CH}_2\text{+H}^+ \text{ minus } H_2O]$
	77	36.0			
	105	74.4		214	OH OH $[(C_6H_5)_2\text{-C-CH}_2\text{+NH}_4^+ \text{ minus } H_2O]^+$
	183	100			$[(C_6H_5)_2\text{-C-OH]}^+$
	183	100		232	OH OH $[(C_6H_5)_2\text{C-CH}_2\text{+NH}_4]^{+\,+}$
	196	--			OH OH $[(C_6H_5)_2\text{-C-CH}_2 \text{ minus } H_2O]^+$

[1]R.A. = relative abundance.
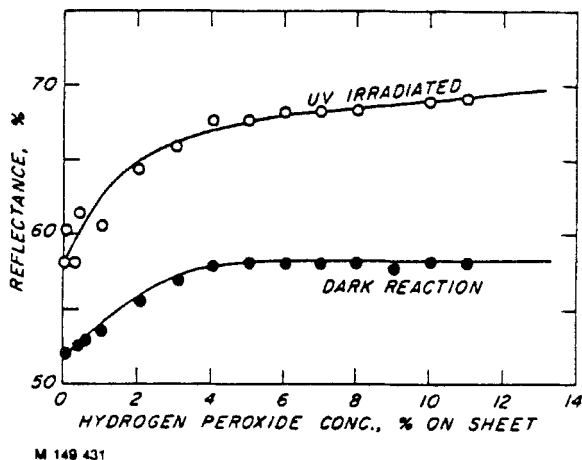
M 149 431

FIGURE 5. Effect of hydrogen peroxide on light-induced bleaching of aspen TMP sheets in MeOH (irradiated 4 h at 45°C; liquor/pulp (g/g) = 12.2). (M149 431)

containing various amounts of water, the sheet reflectance (457 nm) decreased in a regular manner as the water content of the bleaching liquors increased (Figure 6). Benzophenone is not soluble in water and becomes insoluble in methanol when the water content reaches 50%. Uneven bleaching resulted with 50% water content. Hydrogen peroxide was soluble in the bleaching liquors regardless of the amount of water. Bleaching stopped when the water in the methanol reached 72% and 88%, respectively, when benzophenone and hydrogen peroxide were sensitizers. Light-induced brightness reversion, on the other hand, was observed when the water content exceeded these values and in 100% water even when hydrogen peroxide was added prior to irradiation. This particular result with aqueous hydrogen peroxide corroborates Escourrou's finding[22] that UV light does not accelerate hydrogen peroxide bleaching in aqueous solution. Bleaching was retarded possibly because the light-induced auto-oxidation of alcohols was quenched by water. Besides, any methanol peroxide formed in the presence of water was probably converted into formaldehyde and hydrogen peroxide.[23]
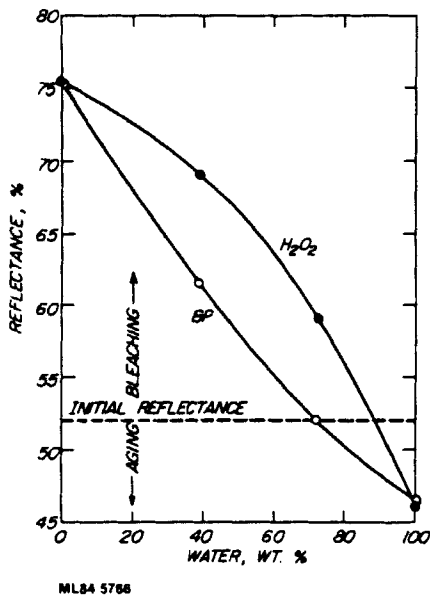
ML84 5766

FIGURE 6. Effect of water to methanol ratio on the light-
induced bleaching of aspen TMP sheets (irradiated 14 h at
39°C; benzophenone (BP)/pulp and H_2O_2/pulp = 13%;
liquor/pulp (g/g) = 12.2; unbleached sheet reflectance -
52%). (ML84 5766)

Alkali.--Aspen TMP sheets bleached less when they were
irradiated while saturated with methanolic sodium hydroxide solu-
tions of benzophenone than when these pulp sheets were irradiated in
methanol-benzophenone solutions (Table 3). This is in contrast to
the improved bleaching obtained when aqueous hydrogen peroxide
solutions are made alkaline. The decreased bleaching was attributed
to decomposition of methanol peroxide by alkali.

UV light.--To determine if the methanol peroxide generated
during irradiation could bleach in the absence of the UV light,
aspen and white oak CMP sheets were heated in the dark with methanol
solutions of this peroxide which had been generated in the absence
of pulp (Table 4). The peroxide was somewhat stable in the

TABLE 3

Effect of Alkali on the Light-Induced Peroxide Production and
Bleaching of Aspen TMP Sheets in Methanol With and Without
Benzophenone (BP) (Irradiated 18.3 h at 45°C;
Benzophenone/Pulp = 6%; Liquor/Pulp (g/g) = 12.2)

Liquor composition	Initial pH[1]	H_2O_2	Handsheet reflectance
		%	%
MeOH + BP	7.2	5.3	68.1
MeOH + BP + NaOH	12.5	2.8	62.6
MeOH	7.2	0.16	58.8
MeOH + NaOH	12.6	0.16	58.6

[1]pH determined after dilution with water.

TABLE 4

Effect of Heat Versus Light on the Residual
Quantity of Peroxide and Bleaching of Aspen
TMP and White Oak CMP Sheets[1]

Pulp	Residual quantity of peroxide (final)	Handsheet reflectance, 457 nm
	micromoles	%
HEATED IN DARK 24 H AT 35°C		
Aspen	261.6	56.8
White oak	293.7	51.6
IRRADIATED 24 H AT 35°C		
Aspen	none	79.5
White oak	55.6	70.6

[1]Unbleached aspen TMP reflectance
51.2%; unbleached white oak CMP reflectance
46.2%; initial quantity of peroxide
387.3 micromoles.

TABLE 5

Effect of UV Light on the Bleaching of White Oak
CMP Sheets in Benzophenol-MeOH (Irradiated 13 h
and 46 h at 30°C; Liquor/Sheet (g/g) = 12.2;
Benzophenone/Sheet (g/g) = 10%)[1]

| Irradiation time | Sheet reflectance, 457 nm | | |
| | Opaque reactor | Glass-windowed reactor | Glass reactor |
		Opaque	Glass	
h	- - - - - - - - - % - - - - - - - - -			
13	--	51.7	67.7	--
46	50.7	60.0	76.4	77.1

[1]Initial reflectance 50.2.

presence of the pulp sheets in the dark since 72% of the original
amount, on the average, remained after 24 h at 35°C. The sheet
reflectance increased only 5 points during heating in the dark.
In contrast, the sheet reflectance increased an average of 26 points
when irradiated during the 24-h period at 35°C. Thus it was con-
cluded that light energy was necessary to accelerate the bleaching
possibly by light-activation of the lignin chromophores and/or
methanol peroxide.

Methanol-benzophenone saturated white oak CMP sheets (0.43 mm
thick) were irradiated in a Kimax glass reactor, in a completely
opaque reactor, and in opaque reactors with Kimax glass windows
that exposed only half of one side of the pulp sheet. After 46-h
irradiation, the reflectance of the sheet in the completely opaque
reactor was unchanged, whereas the reflectance of the sheet in the
all-glass reactor increased 27 points (Table 5). The sheets in the
opaque reactors with glass windows bleached to varying degrees, in
the same time, depending on whether the surface was located behind
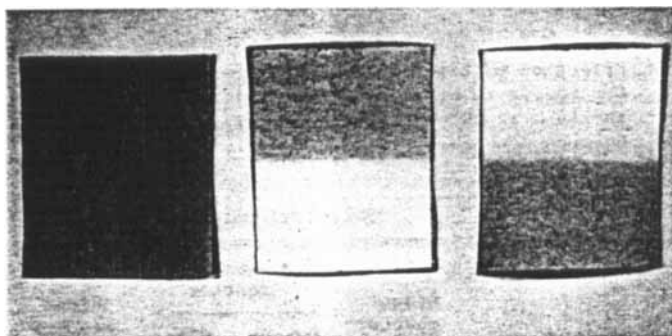the glass or opaque surface. The half of the pulp sheet behind the

FIGURE 7. Effect of UV light on the bleaching of white oak CMP
sheets in MeOH. Left: Sheet before bleaching. Middle and Right:
Sheets after 46 h irradiation (30°C; liquor/pulp (g/g) = 12.2).
The darker half of each bleached sheet was behind the opaque surface
of the reactor; hence, it was exposed only to light which had
passed through the other (exposed) half of the sheet. (M85 002-18)

opaque surface bleached somewhat because the UV light penetrated
the exposed half of the sheet, illuminating the inside of the
photoreactors (Figure 7). This particular experiment shows quanti-
tatively (reflectance, Table 4) and visually (Figure 7) that the
pulp sheets are bleached through the sheet thickness and that
bleaching occurs only where the sheet was irriadated. If there was
significant diffusion of methanol peroxide into the covered area,
it did not react without light activation.

The light-induced bleaching of aspen TMP sheets increased as
the light intensity increased (Figure 8). Since the slopes of the
reflectance versus intensity curves (sensitized and unsensitized)
decreased greatly between about 250 and 750 uW/cm^2, a transition
from easily bleached to a more bleach-resistant chromophore possibly
decreased. However, it appears that additional increases in the
light intensity could result in faster bleaching since the slopes
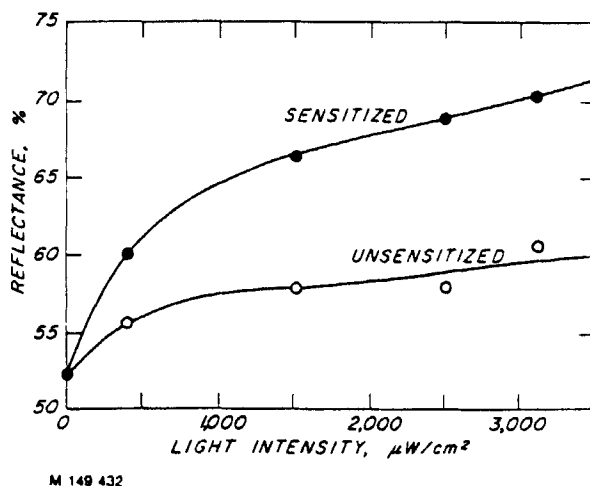of the reflectance versus intensity curves are still positive.

FIGURE 8. Effect of light intensity on the light-induced bleaching of aspen TMP sheets in MeOH with and without benzophenone (BP) (irradiated 30°-45°C for 8 h; BP/pulp = 3%; liquor/pulp (g/g) = 12.2). (M149 432)

POSSIBLE MECHANISMS

Methanol solutions of benzophenone irradiated in the presence of oxygen have produced formaldehyde as detected by a formaldehyde-specific method.[24] In addition, hydrogen peroxide and an organic peroxide have been found in the irradiated solutions by the ceric (IV) and iodometric differential method.[25] During irradiation, the pH of aqueous mixtures of methanol-benzophenone spent liquors decreased to 3.5, indicating the buildup of benzoic acid and formic acid. However, adjusting the pH of the methanol-benzophenone solution to 3.5 with acetic acid prior to irradiation had no effect on light-induced bleaching. When aspen TMP sheets replaced the benzophenone prior to irradiation, a similar drop in the pH of the spent aqueous-methanol liquor was observed. The pulp sheets bleached during irradiation.

TABLE 6

Effect of Singlet Oxygen Quenchers on the Sensitized Light-Induced
Bleaching of Aspen TMP and White Oak CMP Sheets in MeOH (Irradiated
at 45°C; Liquor/Pulp (g/g) = 12.2; 8.6% Benzophenone/Pulp)[1]

DMFn/pulp[2]	DPBF/pulp[3]	DABCO/pulp[3]	Handsheet reflectance, 457 nm
- - - - - - - - - - - - - - - - - - % -			
		ASPEN	
None	--	--	73.0
7.1	--	--	73.0
14.3	--	--	72.5
28.5	--	--	72.0
57.0	--	--	71.0
--	None	None	76.0
--	8.6	--	77.8
--	34.7	--	75.3
--	--	8.6	72.5
--	--	34.7	63.0
--	--	60.6	62.0
		WHITE OAK	
	None	None	66.5
	8.6	--	65.8
	34.7	--	68.8
	--	8.6	63.2
	--	34.7	62.5
	--	60.6	49.9

[1]Unbleached aspen TMP reflectance 53%; unbleached white oak
CMP reflectance 47%.
[2]Irradiated 27 h.
[3]Irradiated 15.5 h.

As discussed previously, the light-induced bleaching rate of aspen TMP sheets was severely retarded when oxygen was displaced from the system by passing nitrogen gas through the photoreactors (Figure 4). Thus oxygen is important to the bleaching reaction(s). Singlet oxygen has been cited for bleaching wood pulps via photo-oxygenation in aqueous alkaline solutions.[26] To test the light-induced bleaching system for the involvement of singlet oxygen, low levels of 2,5-dimethylfuran (DMFn), 1,3-diphenylisobenzofuran (DPBF), and 1,4-diazabicyclo-2,2,2-octane (DABCO), known singlet oxygen quenchers, were added to the methanol solutions of benzophenone prior to irradiating aspen TMP and white oak CMP sheets. DMFn and DPBF quenches singlet oxygen by combining chemically with it; DABCO quenches without reacting with singlet oxygen in methanol.[27-29] Low levels of these quenchers did not inhibit bleaching. When relatively large quantities ($\geq$34.7%/pulp) of DABCO were added, however, bleaching was inhibited substantially. DMFn and DABCO are soluble in methanol solutions of benzophenone forming colorless solutions. DPBF, however, is only slightly soluble in methanol solutions of benzophenone and is yellow-colored. After irradiation for more than 20 hours, DPBF bleached white and remained mostly insoluble. DMFn developed a yellow color during irradiation for the same length of time in the presence and absence of pulp. But the color was washed from the pulp with acetone. DABCO remained colorless when irradiated in the absence of pulp. When pulp was present, however, a dark brown color was formed in the pulp and in the spent bleaching liquor. Apparently DABCO reacted with lignin or lignin degradation products during irradiation. In air-dried pulp sheets DABCO caused discoloration when irradiated with UV light (Table 7). This discoloration probably caused the apparent decrease in bleaching. Therefore it was concluded that singlet oxygen is not important to the light-induced bleaching reactions.

No bleaching occurred when hydrogen peroxide was added to water prior to irradiating pulp sheets (Figure 6). The pulp sheets aged in this case. This eliminated hydrogen peroxide or its photolysis products (i.e., hydroxyl radical) as the bleaching agent(s). But enhanced light-induced bleaching was observed when

TABLE 7

Accelerated Light Aging of Aspen TMP and
White Oak CMP Sheets Treated with
1,4-Diazabicyclo 2,2,2-Octane (DABCO)
(Irradiated Air Dry for 10 h at 35°C)[1]

DABCO/sheet	Handsheet reflectance, 457 nm
- - - - - - - - - - - % - - - - - - - - - - - -	
ASPEN	
None	46.8
6.5	35.2
WHITE OAK	
None	39.8
12.5	31.3

[1]Initial reflectance aspen TMP 53%;
initial reflectance white oak 47%.

aspen TMP sheets were irradiated in methanol solutions of hydrogen
peroxide (Figure 5). Therefore, some photolysis product of hydrogen
peroxide must be responsible for initiating the autooxidation of
methanol forming methanol peroxide.

The addition of known peroxide decomposers, potassium iodide,
ferric acetylacetonate, ferric ammonium sulfate, ferrous ammonium
sulfate, and ferrous sulfate, to the photoreactors prior to irradi-
ating aspen TMP sheets in methanol (Table 8) caused a considerable
decrease in bleaching. These results also indicate that peroxides
are involved in the brightening process.

Because light-induced bleaching is effective only in alcohols,
it does not appear likely that bleaching can be accounted for by
mere autooxidation of the resonance-stabilized phenoxy radicals
generated in lignin during irradiation. Both UV light and methanol
peroxide have been shown to be essential for bleaching to occur.
In addition, it was demonstrated that the UV light and methanol
peroxide must be present at the same time to obtain effective

TABLE 8

Effect of Some Common Peroxide Decomposers
on Light-Induced Bleaching of White Oak
CMP Sheets in MeOH (Irradiated 77 h at
45°C, Additive/Pulp = 10%; Liquor/Pulp
(g/g) = 12.2)

Peroxide decomposer	Handsheet reflectance gain
	%
Potassium iodide	4.7
Ferrous sulfate	4.6
Ferric acetylacetonate	12.9
Ferric ammonium sulfate	10.5
Ferrous ammonium sulfate[1]	6.7
None	25.0

[1]$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$/pulp = 57%;
benzophenone/pulp = 15 pct; irradiated
24 h at 35°C.

bleaching. Further, the relatively large conversion of benzophenone
(about 45%) into 1,1-diphenylglycol (Table 2) during irradiation
indicates that the liquor has a significant quantity of free
radicals such as benzophenone and methanol ketyl radicals. There-
fore, a bleaching mechanism involving the alcohol peroxide reacting
with a light-activated lignin chromophore as shown in scheme 2,
seems a reasonable hypothesis.

EXPERIMENTAL

Sheet Preparation

Aspen TMP and white oak CMP were made into double basis weight
handsheets (120 g/m^2), air dried and cut into 35- by 45-mm rec-
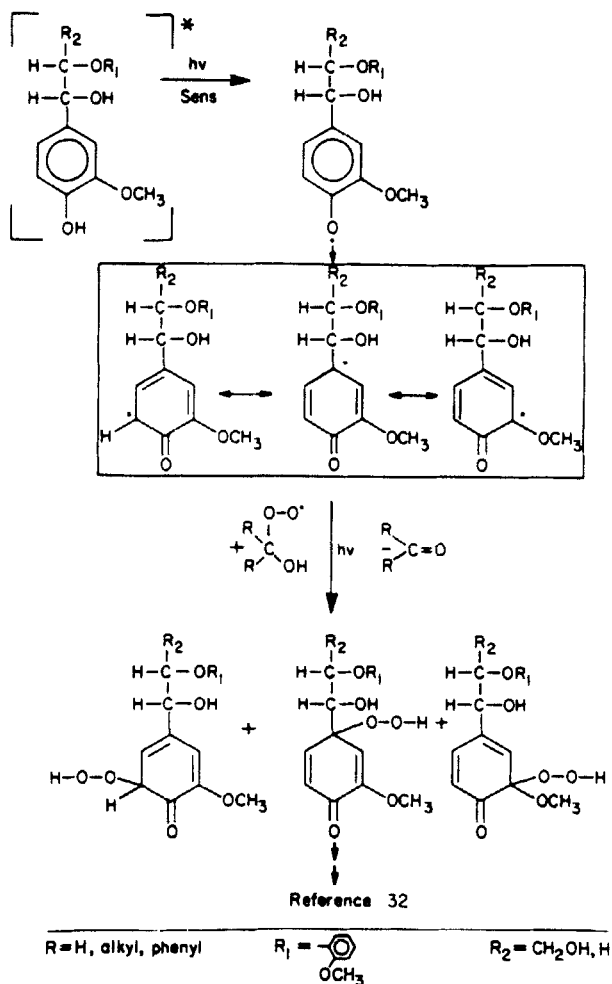
ML84 5698

SCHEME 2. Proposed mechanism for the photooxidative bleaching of free phenolic hydroxyl units in lignin. (ML84 5698)

tangles for subsequent irradiation with near UV light. A portion of the white oak pulp was separated into a fines-free fraction prior to forming sheets. The sheets were stored in the dark to prevent light-induced discoloration.

Sheet Irradiation

Pulp sheets (125-135 mg) were placed in 40- by 80-mm Kimax weighing bottles, and 2 ml of alcohol were added. After adding sensitizer and capping, the bottles were placed in a Rayonet photochemical reactor (model RPR-100) equipped with 16 UV lamps (300-400 nm) and irradiated for appropriate times. The intensity of the light was 3,000 $\mu W/cm^2$. Samples were placed 2 cm from the UV lamps. Some photoreactors were made with inlet and outlet openings so that solvent-saturated gases could flow freely.

UV Intensity Measurement

The UV intensity was determined at 365 nm with a Blak-Ray Long Wave UV meter of Ultraviolet, Inc., San Gabriel, Calif. The meter was calibrated against a standard traceable to the National Bureau of Standards. The effect of infrared (IR) radiation on the 365-nm UV meter reading was removed by using a UV filter on the detector under the same conditions and then correcting for IR contribution.

Reflectance Measurement

The percent reflectance of pulp sheets was determined on a Beckman Model B spectrophotometer equipped with an integrating sphere diffuse reflectance accessory. Both sides of the sheets were read in duplicate at 457 nm using magnesium carbonate as reference. The average values are reported.

Hyrogen Peroxide, Organic Peroxides, and Total Peroxides Determination

Hydrogen peroxide and organic peroxides were determined by a differential analysis on the same sample as developed by Swern.[25] The hydrogen peroxide analysis was also performed by a modified titanium (IV) method[30] as follows:

A standard titanium (IV) solution was prepared by slowly adding ·
titanium (IV) tetrachloride (10 ml) to cold concentrated
hydrochloric acid (50 ml) and then diluting the resulting
yellow solution to 500 ml with distilled water, obtaining
a colorless solution. To 5 ml of this solution was added
aliquots of spent bleaching liquor containing 0.5 to 1.5 mg of
hydrogen peroxide and then diluting the mixture to 25 ml with
5% hydrochloric acid. The absorbance was then measured at
415 nm and the quantity of hydrogen peroxide read from
a calibration curve.

The total peroxides as hydrogen peroxide were determined by
a modified iodometric method for hydrogen peroxide[31] as follows:

The entire spent bleaching liquor was weighed and then
quantitatively transferred to a 250-ml iodine flask and 10 ml
of 6N sulfuric acid, 3 g of potassium iodide in 10 ml water,
five drops of 3% ammonium molybdate solution, and 50 ml of
water were added. The contents of the flask were heated at
65°C for 15 minutes, cooled, and then titrated with 0.1N thio-
sulfate until the brown color of iodine had almost disappeared.
Then 5 ml of starch solution was added and the titration with
thiosulfate continued until the deep blue color disappeared.
After correcting the volume of thiosulfate required for the
sample for the volume required for a blank, the quantity of
peroxides as hydrogen peroxide was calculated.

Methanolic Sodium Hydroxide-Benzophenone Solutions

Solid sodium hydroxide was dissolved in methanol until 2-ml
aliquots of the sodium hydroxide-benzophenone solution gave a pH of
12.5 when dissolved in 10 ml of distilled water.

pH Measurement

Two-ml aliquots of the methanol bleaching solutions were
diluted to 10 ml with distilled water and stirred. Then the pH of
the solutions was determined with a Beckman model 3500 digital pH
meter equipped with a combination electrode. The pH meter was
standardized against an aqueous 6.86 pH buffer solution prior to pH
determination.

Gas Chromatography/Mass Spectrometry (GC/MS)

The components of irradiated methanol solutions of benzophenone were separated and analyzed on a Finnigan 4500 automated gas chromatograph/EI-CI mass spectrometer. A 30-m x 0.252-mm crosslinked fused silica capillary column coated with a nonextractable bonded phase (DB-1) operated at 150°C performed the separation. The column was obtained from J&W Scientific, Inc., and the liquid phase is equivalent to SE30, OV1, and SP-2100. The carrier gas (helium) flow rate was 28 cm per second and the split ratio was 30 to 1. Methane, isobutane, and ammonia were used to effect the chemical ionization of the sample components.

CONCLUSIONS

Hardwood TMP and CMP sheets are bleached when irradiated with near UV light while they are steeped in alcohols in the presence of oxygen. Alcohol peroxides generated during sensitized photo-oxidation of alcohols presumably react with light-activated lignin chromophores producing a brightening effect. The bleaching is enhanced by sensitizers and high light intensity; it is retarded by alkali and water.

Sensitizers activated by light energy initiate the auto-oxidation of alcohols forming bleaching agents. These bleaching agents, which are probably α-hydroxyhydroperoxides, apparently react with light-activated lignin chromophores when irradiated. α-carbonyl groups in lignin probably also function as natural sensitizers.

Although singlet oxygen is presumably generated, it does not appear to be involved in the pulp-brightening reactions.

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