

Brightness reversion of mechanical pulps

VIII. Investigation of synergistic photostabilization methods for high-yield pulp

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Abstract

Recent advances in the photostabilization of mechanical pulp suggest that the use of additive mixtures may provide optimal protection against brightness reversion. Some of the most promising additive mixtures reported in the literature include the use of a UV absorber, such as 2,4-dihydroxybenzophenone, and a radical scavenger. The mechanistic basis of this synergistic effect was explored by monitoring the photostability of benzophenone during brightness reversion. These studies demonstrated that the benzophenone additives were stable under the initial photolysis conditions. The use of mercapto derivatives of benzophenone did not enhance the photostabilization effect, suggesting that the thiol additive and UV absorber need not be in close association with each other for the observed photostabilization effects to occur. © 1997 Elsevier Science S.A.

Keywords: High-yield pulp; Photostabilize; Radical scavenger; UV screens

1. Introduction

Although most high-quality paper is made from lignin-free cellulose fibers, recent advances in pulp manufacturing have yielded writing grades of paper that contain substantial amounts of lignin [1]. The manufacture of this fiber source, commonly referred to as mechanical pulp or high-yield pulp, is attractive due to its efficient utilization of lignocellulosic material. In addition, the bleaching process is lignin retaining and precludes the generation of chlorinated waste products. Unfortunately, paper manufactured from high-yield pulp has limited applications due to its well-known tendency to undergo rapid photoyellowing [2]. Photodiscoloration of mechanical pulp occurs by the absorption of near-UV light by the lignin chromophores present in the pulp. A variety of lignin chromophores are believed to be involved in this process, including diguaiacyl stilbene units, substituted biphenyl structures, coniferyl alcohol end-units and quinone derivatives [3]. Given the variety of chromophores involved in photoyellowing (i.e. brightness reversion), it is not surprising that a complete description of the photoyellowing process is still lacking. Nonetheless, various studies [2,4-6] have substantially improved our knowledge of this process.

Together with the identification of several important chromophores involved in the photoyellowing process, it has become apparent that subsequent radical-based oxidative reactions of lignin phenoxy groups contribute to the overall photoyellowing process [7].

In the light of the proposed mechanisms of brightness reversion, several research groups have begun to develop novel photostabilization strategies for mechanical pulps. The use of antioxidants, such as ascorbic acid [8], mercapto derivatives [9] and formates [10], has shown promising photostabilization properties. As expected, UV absorbers, including 2,4-dihydroxybenzophenone [11], 5-phenylpentadienoic acid [12] and triazole derivatives [13], have also been shown to be effective at retarding the brightness reversion of mechanical pulps, although at application levels generally considered to be too high to be of use for commercial applications.

Recently, Davidson et al. [14] and Pan et al. [12] have shown that the use of additive mixtures can result in photostabilization effects which are substantially better than those achieved with individual additives. The use of thiol radical scavengers in combination with 2,4-dihydroxybenzophenone has been shown to be an exceptionally promising mixture. As illustrated in Fig. 1, the use of ethylene glycol bishthioglycolate and 2,4-dihydroxybenzophenone retards the photoy-

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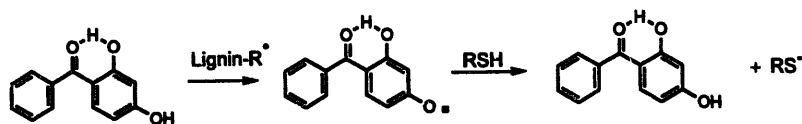


Fig. 1. Photoyellowing properties of untreated and treated BCTMP hardwood test sheets.

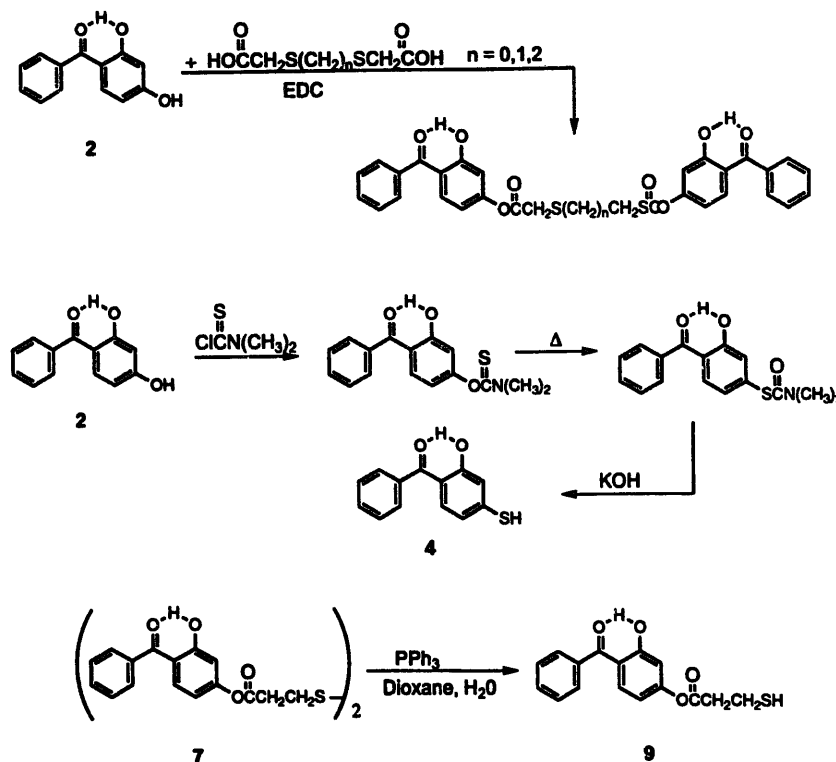


Fig. 2. Proposed photostabilization mechanisms for 2,4-dihydroxybenzophenone derivatives.

ellowing properties of bleached chemithermomechanical pulp (BCTMP) such that to achieve comparable levels of photostabilization with a single additive would require more than a threefold increase in additive application levels. Davidson et al. [14] have recently proposed that the improved photostabilization effect of 2,4-dihydroxybenzophenone when combined with thiol additives is due to the thiol additive acting as a reductant for 2,4-dihydroxybenzophenone (see Fig. 2). It has been proposed that the 2,4-dihydroxybenzophenone acts not only as a UV absorber, but also as a radical scavenger (Fig. 2, step 1) and, in the presence of a good reducing agent, such as thiol additives, the benzophenone radical is reduced. This mechanism explains the synergistic effects observed for 2,4-dihydroxybenzophenone and thiol co-additives. This paper summarizes our investigations of the chemical mechanisms contributing to the observed synergistic effects for additive mixtures.

2. Results

2.1. Materials and methods

Methylenebis(mercaptoacetic acid) was purchased from Lancaster Synthesis and ethylenebis(mercaptoacetic acid) was purchased from TCI America Inc. The methyl esters of these bis-sulfides were prepared using simple Fisher esteri-

fication and were used without any further purification. All other reagents were purchased from Aldrich Chemical Co., Milwaukee, WI, and were used as received. All nuclear magnetic resonance (NMR) spectra were run on a Bruker Avance 400 MHz spectrometer. NMR data are reported as parts per million and were run in CDCl_3 . Fourier transform IR (FTIR) data are reported as reciprocal centimeters (intensity), UV data are reported as nanometers (absorbance) and melting points (m.p.) are reported uncorrected. A commercial BCTMP, manufactured from aspen, was employed for the studies described in this report. All pulp samples were disintegrated using only glass or Teflon labware to prevent metal contamination. After disintegration, the pulps were Soxhlet extracted with acetone for 24 h and allowed to air dry for 24 h in a controlled 50% humidity environment. Previous studies have demonstrated that this mild extraction procedure does not influence the brightness reversion properties of mechanical pulp, but allows the accurate determination of additive application levels and simplifies post-photolysis additive studies [15]. BCTMP test sheets were prepared following standard literature methods [16]. Brightness measurements were recorded following standard TAPPI methods [17]. This procedure basically determines the percentage light reflectance for a light source centered at 457 nm.

2.2. General method for application of additive onto BCTMP test sheets

In a typical experiment, BCTMP test sheets were weighed in a constant 50% humidity atmosphere. The additives were applied to the test sheets with a TLC sprayer at 1 and 2 wt.% levels using methanol. The test sheets were then dried at a constant 50% humidity and reweighed to ensure correct additive levels. All levels agreed to within $\pm 5\%$.

2.3. General photolysis procedure for treated and untreated BCTMP test sheets

In a typical experiment, BCTMP test sheets were attached to a merry-go-round and photolyzed in a Rayonet photochemical reactor (model number RPR-100) equipped with eight RPR 3500 Å lamps and a cooling fan with a reaction temperature of 35–40 °C. At selected time periods, the test sheets were removed from the reactor, kept in the dark and equilibrated in the temperature and humidity conditions of the optical testing room. After recording the optical reflectance properties, the test sheets were placed in the Rayonet reactor and photolyzed further.

2.4. Synthesis

2.4.1. 2-Hydroxy-4-mercaptobenzophenone (4) [18]

A solution of 200 ml of anhydrous *N,N*-dimethylformamide (DMF), 4.28 g (0.020 mol) of 2,4-dihydroxybenzophenone and 4.51 g (0.040 mol) of 1,4-diazabicyclo[2.2.2]octane (DABCO) was cooled to 4 °C under argon. Next, 3.09 g (0.025 mol) of dimethylthiocarbonyl chloride was added to the cold stirred solution. The reaction was allowed to warm to room temperature and was heated for 14 h at 50 °C. The entire reaction solution was then poured into 1 l of water and extracted with CH_2Cl_2 (4 \times 150 ml). The methylene chloride extracts were dried over magnesium sulfate, filtered and rotary evaporated to 5.54 g of yellow oil. This oil was purified on a silica gel plug (30 cm \times 5 cm) using CH_2Cl_2 -MeOH (95 : 5) to yield 1.80 g of yellow crystals of 2-hydroxy-4-dimethylthiocarbonylbenzophenone. These crystals were then added to 10.0 g of tetramethylene sulfone, and the mixture was heated under argon at 240 °C for 40 min. The dark reaction mixture was cooled to room temperature, poured into 75 ml of water and extracted with ethyl ether (3 \times 50 ml). The ether extracts were dried over MgSO_4 , filtered and reduced to a yellow solid. This yellow solid was recrystallized in 20 ml of MeOH to yield 1.73 g of yellow crystals. ^1H NMR and FTIR analysis indicated that the crystals were the desired 2-hydroxy-4-dimethylthiocarbonylbenzophenone.

The product was then refluxed under argon in 6 N KOH- H_2O for 10 h. The reaction was neutralized (pH 8) and extracted with ethyl ether (3 \times 250 ml). The ether extracts were dried over MgSO_4 , filtered, rotary evaporated and dried under vacuum to yield 1.07 g of a yellow solid. This yellow

solid was recrystallized under argon using 70 ml of MeOH- CH_2Cl_2 (2.5 : 1) that had been rigorously purged with argon before use. Recrystallization yielded 0.88 g of yellow powder. The yellow powder was titrated using the Ellman's reagent [19] test and a UV spectrophotometer to measure the absorbance at 412 nm. The powder proved to be 94% thiol and 6% disulfide. The UV λ_{max} value at 333 nm tailed into the visible and precluded its use as a brightness reversion preventative agent. Calculated: C, 67.80%; H, 4.38%; S, 13.92%. Found: C, 66.45%; H, 4.50%; S, 14.10%. ^1H NMR: 12.28 (s, 1H), 7.57 (m, 6H), 6.93 (d, $J = 1.8$ Hz, 1H), 6.69 (d, $J = 6.5$ Hz, 1H), 3.65 (s, 1H). ^{13}C NMR: 200.01, 166.28, 165.44, 138.22, 135.28, 131.46, 128.83, 128.29, 113.13, 107.62, 101.52, 67.28, 33.19, 29.27, 27.60. FTIR: 3194(w), 3078(w), 2925(w), 2558(w), 1623(m), 1594(m), 1572(m), 1415(m), 1344(s), 799(m), 1082(m). UV λ_{max} : 333 (0.674), 302 (1.693), 251 (1.355) 210 (2.459) at 0.0005 M.

The three coupling reactions were carried out using the same general procedure. The general procedure and analytical data for the two other coupled benzophenones are given below.

2.4.2. Bis(2-hydroxy-4-(methylenebis(mercaptoaceto))-benzophenone) (5)

A mixture of anhydrous tetrahydrofuran (THF) (10 ml), anhydrous CH_2Cl_2 (150 ml) and 2.23 g (0.011 mol) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was stirred under argon and cooled to 0 °C. A solution of 1.96 g (0.010 mol) of methylenebis(mercaptoacetic acid) in 50 ml of anhydrous THF was added dropwise to the stirred mixture over 1 h. The reaction mixture was allowed to warm to room temperature and a solution of 25 ml of anhydrous THF, 25 ml of anhydrous CH_2Cl_2 and 4.28 g (0.020 mol) of 2,4-dihydroxybenzophenone was added dropwise with stirring over 1 h. The reaction was stirred at room temperature for 24 h and rotary evaporated to leave a yellow oil. This oil was dissolved in 100 ml of CH_2Cl_2 , washed with water (2 \times 100 ml), dried over Na_2SO_4 and filtered. The filtrate gave three spots on thin layer chromatography (TLC) (100% CH_2Cl_2 on silica), with the fastest eluting spot being the desired coupled product. The CH_2Cl_2 filtrate was rotary evaporated to a pale yellow oil which was run through a flash column (100% CH_2Cl_2) to yield 2.22 g (37% yield) of the desired linked benzophenone-bis-sulfide (m.p. 127–129 °C). Calculated: C, 63.25%; H, 4.11%; S, 10.89%. Found: C, 63.15%; H, 4.15%; S, 10.98%. ^1H NMR: 12.33 (s, 2H), 7.44 (m, 12H), 6.45 (s, 2H), 6.33 (s, 2H), 4.07 (s, 4H), 3.89 (s, 2H). ^{13}C NMR: 200.68, 167.59, 164.85, 156.35, 137.84, 134.88, 132.05, 129.86, 128.45, 117.43, 112.22, 111.04, 36.70, 32.26. FTIR: 3090 (w), 2979(w), 2853(w), 1748(vs), 1624(vs), 1343(s), 1247(vs), 1227(vs), 1116(vs), 1101(vs), 980(s), 773(m).

698(s). UV λ_{max} : 333.0 (0.626), 268.0 (1.940) at 0.0005 M.

2.4.3. Bis(2-hydroxy-4-(ethylenebis(mercaptoaceto))-benzophenone) (6)

White crystals, 2.24 g (37% yield), m.p. 131–133 °C. Calculated: C, 63.77%; H, 4.49%; S, 10.64%. Found: C, 63.68%; H, 4.43%; S, 10.67%. ¹H NMR: 12.27 (s, 2H), 7.57 (m, 12H), 6.83 (s, 2H), 6.65 (d, $J=8$ Hz, 2H), 3.52 (s, 4H), 3.08 (s, 4H). ¹³C NMR: 200.72, 167.87, 156.27, 137.64, 132.12, 129.08, 117.29, 112.30, 111.02, 33.46, 31.99. FTIR: 3090(w), 2979(w), 2923(w), 1748(s), 1624(vs), 1606(vs), 1504(m), 1343(s), 1247(vs), 1227(vs), 1116(s), 1111(s), 980(m), 698(s). UV λ_{max} : 329 (0.569), 268 (1.464), 216 (2.224) at 0.0005 M.

2.4.4. Bis(2-hydroxy-4-(bis(3,3-mercaptopropionyl))-benzophenone) (7)

White crystals, 1.80 g (31.9% yield), m.p. 88–89.5 °C. Calculated: C, 63.77%; H, 4.35%; S, 10.64%. Found: C, 63.66%; H, 4.32%; S, 10.59%. ¹H NMR: 12.41 (s, 2H), 7.55 (m, 12H), 6.77 (s, 2H), 6.58 (d, $J=8$ Hz, 2H), 3.02 (t, $J=4$ Hz, 2H), 2.93 (t, $J=4$ Hz, 2H). ¹³C NMR: 200.05, 169.05, 165.04, 157.12, 137.50, 135.33, 132.43, 129.44, 128.79, 112.93, 111.36, 34.63, 33.26. FTIR: 3101(w), 3058(w), 2919(w), 1753(s), 1627(s), 1582(s), 1492(m), 1333(m), 1210(s), 1165(s), 1153(s), 1117(vs), 986(s), 904(s), 702(s). UV λ_{max} : 330 (0.626), 268 (1.579), 216 (1.94).

2.4.5. 2-Hydroxy-4-(4-mercaptoputoxy)benzophenone (8)

A solution of 150 ml of THF, 20 ml of water, 1.68 g of potassium hydroxide and 6.427 g (0.030 mol) of 2,4-dihydroxybenzophenone was stirred under argon for 1 h. Then 1,4-dibromobutane was added and the reaction mixture was refluxed for 24 h. The reaction mixture was rotary evaporated to an oily mixture. This mixture was dissolved in CH₂Cl₂ and filtered. The organic layer was saved and dried over MgSO₄. The organic layer was then rotary evaporated to a yellow oil, which was washed with hexane, and the remaining solid was chromatographed on a silica gel plug (4 cm × 12 cm) with 100% CH₂Cl₂. The first 500 ml was discarded, and the next 1 l was collected and reduced under vacuum to leave a white–yellow solid (m.p. 70–72 °C). This solid was chromatographed again on a 4 cm × 25 cm column with CH₂Cl₂–hexane (50 : 50) as eluent to yield 3.44 g of the desired 2-hydroxy-4-(4-bromobutoxy)benzophenone (m.p. 81–82 °C; 87 °C [20]). This solid was dissolved in methanol, cooled to 10 °C and an aqueous solution (30 ml) of 0.1 M trithiocarbonate (NaSC(S)SNa) was added to the cold methanolic reaction mixture. The mixture was allowed to warm to room temperature and was stirred for 12 h under argon. The reaction mixture was then neutralized to pH 7 with 1.0 M HCl, and the methanol/CS₂ was removed under vacuum at room temperature. The aqueous phase was extracted with ethyl ether (3 × 150 ml), and the ether extracts were dried over MgSO₄.

The ether was removed using a rotary evaporator to leave 3.11 g of waxy yellow solid. This solid was chromatographed using a gradient elution from 100% hexane to 50 : 50 CH₂Cl₂–hexane on a silica gel column (4 cm × 25 cm). An off-white solid (1.84 g, m.p. 68–72 °C) was obtained, which proved to be the desired compound. The compound appeared to be completely pure to gas chromatography (GC), but titration with Ellman's reagent indicated that the solid was 92.5% thiol with the rest being the disulfide. ¹H NMR: 12.65 (s, 1H), 7.56 (m, 6H), 6.47 (s, 1H), 6.38 (d, $J=4$ Hz, 1H), 4.03 (t, $J=8$ Hz, 2H), 3.05 (m, 2H), 1.95 (m, 2H), 1.5 (broad s, 1H). ¹³C NMR: 200.00, 166.28, 166.43, 138.22, 135.28, 131.46, 128.83, 128.29, 113.12, 107.62, 101.52, 67.28, 33.19, 29.27, 27.60.

2.4.6. 2-Hydroxy-4-(3-mercaptopropionyl)benzophenone (9)

This compound proved to be impossible to synthesize using the modified EDC procedure, and so a literature procedure for the mild reduction of alkyl sulfides was used [21]. A dioxan–water solution (50 : 50, 150 ml) was purged with argon for 4 h. To this solution, previously synthesized 7 (1.50 g, 0.0025 mol), 0.05 g of ethylenediaminetetraacetic acid (EDTA), 0.1 g of NaCl and 7.5 ml of 0.1 N HCl were added. Then 1.31 g (0.005 mol) of triphenylphosphine was added, and the reaction was warmed to 40 °C for 2 h and then cooled to room temperature. The reaction was poured into 100 ml of ethyl ether and 100 ml of water, and the organic layer was saved. The organic phase was washed with water (100 ml), dried over MgSO₄ and filtered. The organic layer was dried under vacuum to leave 1.85 g of a white solid. This solid was chromatographed on a 4 cm × 25 cm column using silica gel and CH₂Cl₂–hexane (30 : 70) as eluent. White waxy crystals (1.23 g, m.p. 37–40 °C) were obtained. Calculated: C, 63.56%; H, 4.67%; S, 10.60%. Found: C, 63.58%; H, 4.66%; S, 10.50%. ¹H NMR: 12.30 (s, 2H), 7.52 (m, 12H), 6.77 (s, 2H), 6.60 (d, $J=2.4$ Hz, 2H), 2.82 (m, 4H), 1.65 (t, $J=8.0$ Hz, 3H). ¹³C NMR: 202.39, 170.98, 166.40, 158.00, 139.44, 136.73, 130.71, 130.09, 118.82, 40.22, 21.23. FTIR: 3058(w), 2954(w), 2570(w), 1750(vs), 1628(vs), 1579(s), 1495(s), 1335(vs), 1244(vs), 1133(vs), 1107(vs), 976(s), 912(s), 699(vs). UV λ_{max} : 330 (0.640), 268 (1.477), 215 (1.95) at 0.0005 M.

2.4.7. 2-Hydroxy-4-propionylbenzophenone (10)

An anhydrous THF solution (150 ml), potassium carbonate (0.57 g) and 2,4-dihydroxybenzophenone (4.28 g, 0.020 mol) solution were stirred under argon for 1 h. Then propionyl chloride (2.00 g, 0.020 mol) was added, and the reaction was refluxed under argon for 24 h. The reaction mixture was then filtered and rotary evaporated to a viscous clear oil. This oil was dried on a vacuum pump for 72 h and then chromatographed on a 4 cm × 24 cm silica gel column with hexane–CH₂Cl₂ (50 : 50) as eluent. Fractions 10–21 (25 ml) were collected and combined to yield 4.46 g of the desired product as an oil, which proved to be 98.7% pure by GC.

Table 1
 Brightness changes and product analysis of benzophenone-treated BCTMP and cellulose test sheets irradiated with near-UV light ^a

Additive applied ^b /matrix	Period of irradiation (h)	Photostabilization effect ^c	Benzophenone recovery ^d
2-Hydroxy-4-methoxybenzophenone (1)			
BCTMP	0	–	99.9 +
	2	52.8	99.9 +
	4	52.4	99.9 +
	8	52.4	98.3
	64	30.8	98.8
Cellulose	0	–	99.9
	64	–	99.0
2,4-Dihydroxybenzophenone (2)			
BCTMP	0	–	99.9 +
	2	85.2	99.5
	4	84.5	98.8
	8	81.0	98.6
	64	66.3	86.7
Cellulose	0	–	99.5
	64	–	98.9
2-Hydroxybenzophenone (3)			
BCTMP	0	–	99.9 +
	2	62.5	99.0
	4	32.0	92.6
	8	11.1	92.3
	64	23.3	92.0
Cellulose	0	–	99.9
	64	–	99.1

^a Test sheets irradiated with light wavelengths of 300–400 nm and maximum output at approximately 350 nm.

^b Additives were applied onto test sheets on a 3 wt.% additive/wt test sheet basis.

^c Photostabilization effect = [(change in brightness for treated test sheet) – (change in brightness for untreated test sheet)] / (change in brightness for untreated test sheet) (%); brightness changes were monitored by measuring the percentage of reflectance light centered at 457 nm following standard methods.

^d Percentage benzophenone recoveries were determined by extended Soxhlet extraction and characterization of the extracts by GC/MS, ¹H NMR and TLC; in all cases, only starting material was detected in the extracts.

¹H NMR: 12.19 (s, 1H), 7.50 (m, 6H), 6.76 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 2.54 (q, *J* = 6 Hz, 2H), 1.18 (t, *J* = 8 Hz, 3H). ¹³C NMR: 200.73, 172.10, 164.76, 157.80, 134.05, 134.81, 131.98, 129.05, 128.41, 125.87, 112.62, 110.08, 27.80, 8.92. UV λ_{\max} : 326 (0.728), 274 (1.048), 207 (1.844) at 0.0005 M.

3. Discussion

During our initial investigation on the optimization of the use of additive mixtures for mechanical pulps, we explored the mechanisms contributing to the observed synergistic effects. The principal photostabilization mechanism of most benzophenone derivatives involves the absorption of near-UV light and the dissipation of this energy in a manner which does not lead to photosensitization. The light stability of these UV absorbers is attributed to the fast non-radiative decay mechanism from the excited state to the ground state, which has been shown to be due to the internal hydrogen bond between the two hydroxy groups and the carbonyl group. Despite this efficient photostabilization mechanism, it is well known that, for some plastic applications, 2-hydroxybenzophenone derivatives act as UV absorbers and radical scavenger agents in a manner similar to that described in Fig. 2

[22]. The synergistic effects noted with thiol additives and benzophenone derivatives in mechanical pulp may therefore be reasonably attributed, in part, to a protective radical scavenging mechanism. To investigate the likelihood of this mechanistic interpretation, we applied a series of benzophenone derivatives to BCTMP test sheets, including 2-hydroxy-4-methoxybenzophenone (1), 2,4-dihydroxybenzophenone (2) and 2-hydroxybenzophenone (3). The results of photolysis of the BCTMP and cellulose test sheets are summarized in Table 1.

After irradiation, each test sheet was Soxhlet extracted, and the extracts were spectroscopically characterized. In each case, product analysis of the extracts indicated that only the starting material was present, and the yields were greater than 99% for the first 2 h of irradiation of the BCTMP test sheets. After irradiation for 8 h, all three benzophenone derivatives were recovered from BCTMP in greater than 90% yield with benzophenone 3 affording the lowest recovery yield of 92.6%. On prolonged photolysis for 64 h, 2,4-dihydroxybenzophenone impregnated on BCTMP appeared to suffer the greatest loss of starting material (i.e. 13.3% starting material lost). Although no oxidative products were detected in the extracts, this probably occurs due to radical coupling reactions with either lignin and/or polysaccharides in the pulp. These results extend the recent report by Trichet et al. [23],

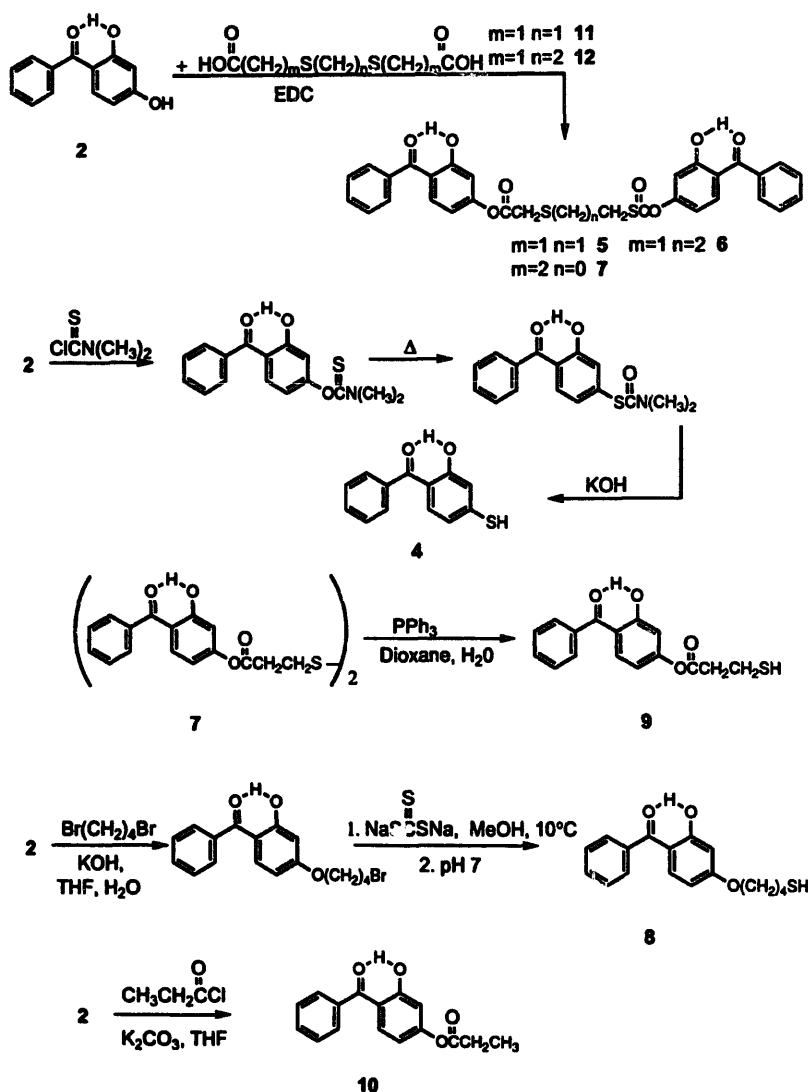


Fig. 3. Synthetic methodology employed for the synthesis of 4-substituted benzophenone derivatives.

who concluded that methyl-3-hydroxy-4-benzoylphenoxyacetate impregnated on mechanical pulp is relatively stable on irradiation.

Control experiments using cellulose as a support matrix indicated that the three benzophenones did not degrade in the absence of lignin. This result suggests that the loss of benzophenone applied to BCTMP is not due to direct photochemical reactions, but mainly due to post-photolysis reactions involving reactive lignin fragments. In summary, these results indicate that, in the early phase of brightness reversion of mechanical pulp, little loss of benzophenone occurs due to photoinitiated degradation reactions, but on prolonged exposure to light, small amounts of the UV screen are consumed. The studies highlighted in this report suggest that the degradation of benzophenone derivatives during the photolysis of mechanical pulp is a slow process and certainly does not play a dominant role in the early phase of photoaging. In turn, the results indicate that the synergistic effects observed for thiol and benzophenone additives do not directly involve a thiol-based benzophenone regeneration mechanism

as summarized in Fig. 2 in the early phase of the photoaging process. These results are also consistent with thermodynamic considerations, which suggest that the phenols should scavenge thiyl radicals [24] and hence would not regenerate benzophenone radicals.

To determine whether or not there is a beneficial effect in having the radical scavenger in close association with the UV absorber, we synthesized a series of novel benzophenone derivatives incorporating an antioxidant functional group into the molecule. The incorporation of an antioxidant functionality into a UV absorber has been successfully utilized to improve the photostability of several polymer antioxidants [25]. Employing modern synthetic methods, we had envisaged the incorporation of a thiol group, a bismethylene disulfide (RSCH_2SR), a bisethylene disulfide ($\text{RSCH}_2\text{CH}_2\text{SR}$) or disulfide, each attached to the 4 position of benzophenone. Each of these sulfur functional groups has been shown previously to be an effective photostabilization agent for mechanical pulp. Fig. 3 summarizes the synthetic methodology employed for these studies.

Our initial synthetic target was to obtain the 4-thiol derivative of 2,4-dihydroxybenzophenone, which was readily prepared by treating **2** with dimethylthiocarbonyl chloride; subsequent Newman–Kwart rearrangement and hydrolysis yielded **4** (see Fig. 3). Unfortunately, the resulting product had a significant absorption in the visible range, thereby precluding its use as a photostabilization agent. Clearly, the additional electron-donating tendency of the thiol group shifted the absorption spectrum of **4** into the visible range. To preclude this effect, the sulfur antioxidants were attached to 2,4-dihydroxybenzophenone by means of an ester or ether linkage at the 4-hydroxy group. The condensation reaction to form the ester was achieved by employing EDC and the appropriate diacid as shown in Fig. 3.

The brightness stabilization properties of the benzophenone derivatives **5–7** were compared with the photostabilization properties of the 4-alkyl-substituted benzophenone derivatives **1** and **9** and the sulfur-based antioxidants. The results of these studies are summarized in Fig. 4. The photoyellowing studies of the “linked” additives and related precursors demonstrate that the sulfur-linked benzophenone additives do not retard the photoyellowing of mechanical pulp any more than the benzophenone additives **1** and **9**. These results suggest that the attachment of the sulfur group to the benzophenone unit is not beneficial. This conclusion was further confirmed by treating test sheets of BCTMP with molar equivalents of the benzophenone **1**, dimethyl esters **11** and **12**, benzophenones **5–8** or combinations of benzophenone **1** and the dimethyl esters **11** and **12**. The resulting BCTMP test sheets were photolyzed, and at selected time periods the percentage reflectance values for the irradiated test sheets were recorded. Fig. 5 summarizes the results of these photolysis studies and, in each case, the unlinked additive mixture provides the best photostabilization effect. Repeating this experimental procedure with benzophenone **3** and the corresponding “unlinked” additives **1** and ethyl 3-mercaptopropionate demonstrated that the best photostabilization

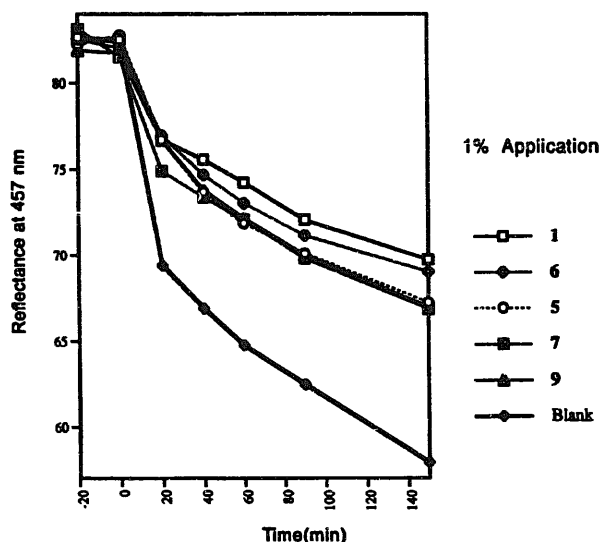


Fig. 4. Photoyellowing properties of BCTMP hardwood test sheets treated with benzophenone derivatives **1**, **5**, **6** and **7**.

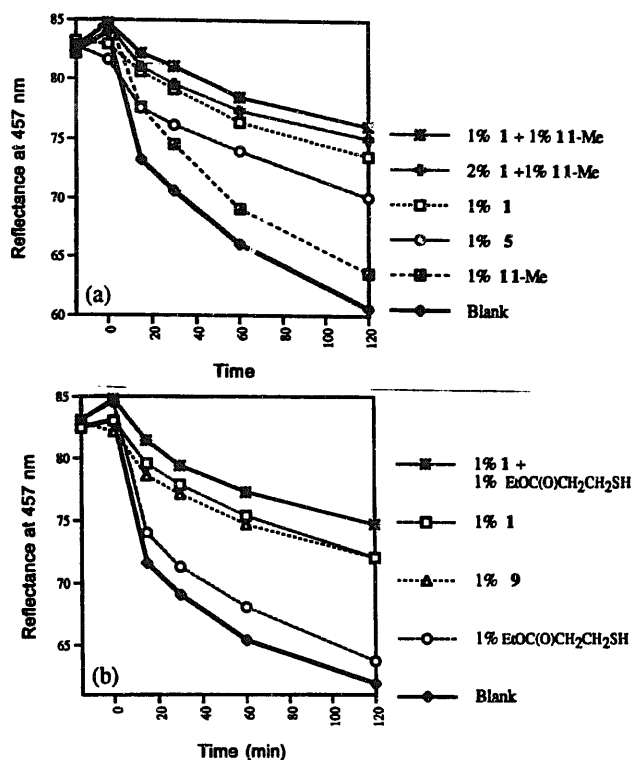


Fig. 5. Comparative photoyellowing properties of BCTMP hardwood test sheets treated with benzophenone derivatives **1**, **5**, **9** and **(1+11)** and **(1+12)**.

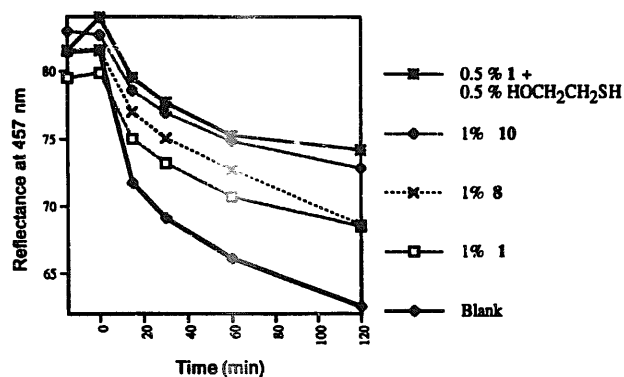


Fig. 6. Comparative photoyellowing properties of BCTMP hardwood test sheets treated with benzophenone derivatives **1**, **8**, **9** and **(1+HOCH₂CH₂SH)**.

effects occurred when the benzophenone and mercapto additives were added as separate compounds to the BCTMP test sheet, as shown in Fig. 6. Previous studies by Pan et al. [12] have demonstrated that the use of additive mixtures provides a distinct advantage in retarding the overall rates of brightness reversion.

A comparison of the UV absorbance of 2,4-dihydroxybenzophenone (**3**) (UV λ_{\max} = 322 nm), 2-hydroxy-4-methoxybenzophenone (**1**) (UV λ_{\max} = 323 nm), 2-hydroxy-4-propionylbenzophenone (**10**) (UV λ_{\max} = 326 nm) and 2-hydroxy-4-(4-mercaptoputoxy)benzophenone (**8**) (UV λ_{\max} = 314 nm) shows little difference in absorbance in the 300–400 nm range (all had approximately the same absolute absorbance in this range). Therefore the differences in pho-

tostabilization between linked and unlinked additive mixtures are not due to UV absorbance changes, but to the blocking of the 4-phenolic site on benzophenone with the additives.

In each case, the linked additives had either the same or decreased photostabilization ability compared with the unlinked additives. The results of these investigations suggest that there is no intrinsic benefit in having the sulfur-based antioxidant closely associated with the UV absorber absorbed on the BCTMP fiber.

4. Conclusions

Product analysis studies of photolyzed benzophenone-treated BCTMP test sheets indicate that, in the initial photoaging process, little if any benzophenone is lost due to thermal/photochemical degradation. This suggests that the beneficial effects of thiol and benzophenones for the photostabilization of mechanical pulp are not due to a simple synergistic regeneration mechanism. Although our data do not preclude this type of reaction from occurring later in the photoaging process, the results summarized in Table 1 suggest that it is not an important factor contributing to the lifetime of benzophenone during photolysis. Presumably, the observed photostabilization effects occur, in part, by the reduction in the overall flux of light transmitted onto the pulp by the benzophenone derivatives and a combination of radical scavenging reactions and nucleophilic addition reactions occurring with the sulfur additives and the lignin chromophores in the pulp. The mechanism of photoyellowing of mechanical pulp involves several interrelated chemical pathways, and any successful photostabilization technology will need to address a variety of photoyellowing pathways. To date, the best means of addressing this multicomponent oxidative reaction mechanism has been to employ several additives that operate on different components of the overall brightness reversion phenomenon.

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