Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 631

Brightness Reversion of Mechanical Pulps VIII: Investigation of Synergistic Photostabilization Methods for High-Yield Pulp

C.M. Cook and A.J. Ragauskas

January 1997

Submitted to
J. Photochem. Photobiol.

Copyright© 1997 by the Institute of Paper Science and Technology

For Members Only

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and

- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and

- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

The Institute of Paper Science and Technology assures equal opportunity to all qualified persons without regard to race, color, religion, sex, national origin, age, disability, marital status, or Vietnam era veterans status in the admission to, participation in, treatment of, or employment in the programs and activities which the Institute operates.

Brightness reversion of mechanical pulps VIII: Investigation of synergistic photostabilization methods for high-yield pulp

C. M. Cook and A. J. Ragauskas*

Institute of Paper Science and Technology
Atlanta, GA, USA
30318

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.

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

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]. This fiber source, commonly referred to as mechanical pulp or high-yield pulp, is an attractive manufacturing process 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 comes about by absorption of near-UV light by 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, studies by Heitner [2], Castellan [5], Gellerstedt [4], and others [6] have substantially improved our knowledge of this process. Along with identifying several important chromophores involved in the photoyellowing process, it has become apparent that subsequent radical-based oxidative reactions of lignin phenoxy groups contributed to the overall photoyellowing process [7].

In 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 to be 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, Castellan [14] and Ragauskas [12] have shown that the use of additive mixtures can result in photostabilization effects that are substantially better than those that can be achieved with individual additives. The use of thiol radical scavengers in combination with 2,4-dihydroxybenzophenone was shown to be an exceptionally promising mixture. As shown in Figure 1, the use of ethylene glycol bisthioglycolate and 2,4-dihydroxybenzophenone retarded the photoyellowing 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. Castellan [14] has recently proposed that the improved photostabilization effect of 2,4-dihydroxybenzophenone when combined with thiol additives was due to the thiol additive acting as a reductant for 2,4-dihydroxybenzophenone (see Fig. 2). It was proposed that the 2,4-dihydroxybenzophenone acted 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 into the chemical mechanisms that contribute to the observed synergistic effects for additive mixtures.

2. Results

2.1 Materials and methods

The methylenebis(mercaptoacetic acid) was purchased from Lancaster Synthesis, and the ethylenebis(mercaptoacetic acid) was purchased from TCI America Inc. Methyl esters of these bissulfides were prepared using a simple

Fisher esterification and were used as is with no further purification. All other reagents were purchased from Aldrich Chemical Co., Milwaukee, WI, and used as received. All NMR spectra were run on a Bruker Avance 400 MHz NMR. NMR's are reported as ppm and were run in $CDCl_3$, FTIR reported as cm^{-1} (intensity), and UV data reported as nm(Absorbance), and Mp's are reported uncorrected. A commercial bleached chemithermomechanical pulp [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 for 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 % 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 using a TLC sprayer at one and two weight % 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 +/- 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 photolyzed in a Rayonet Photochemical Reactor (Model Number: RPR-100) equipped with eight RPR 3500 A 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 with 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 further photolyzed.

2.4 Synthesis

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

A solution of 200 mL anhydrous DMF, 4.28 g (0.020 mole) 2,4-dihydroxybenzophenone, and 4.51 g (0.040 mole) 1,4-diazabicyclo[2.2.2]octane

(DABCO) was cooled to 4°C under argon. Next, 3.09 g (0.025 mole) of dimethylthiocarbamoylchloride was added all at once to the cold stirring solution. The reaction was allowed to warm to rt 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 (4x150 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 x 5 cm) using CH_2Cl_2/MeOH (95/5) to yield 1.80g of yellow crystals of 2-hydroxy-4-dimethylthiocarboylbenzophenone. Next, these crystals were added to 10.0 g of tetramethylene sulfone, and the mixture was heated under argon at 240°C for 40 minutes. The dark reaction mixture was cooled to rt, poured into 75 mL water, and extracted with ethyl ether (3x50 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 1.73g of yellow crystals. ^{1}H NMR and FTIR analysis indicated that the crystals were the desired 2-hydroxy-4-dimethylcarbothiobenzophenone.

Next, the product was refluxed under argon in 6 N KOH/H_2O for 10h. The reaction was neutralized (pH~8) and extracted with ethyl ether (3 x 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 rigourosly purged with argon before using. The recrystallization yielded 0.88 g of yellow powder. The yellow powder was titrated using Ellman's reagent [19] test and a UV spectrophotometer to measure absorbance at 412 nm. The powder proved to be 94% thiol and 6% disulfide. The UV λ max at 333 nm tailed into the visible and precluded its use as a brightness reversion preventative agent. Calcd. % C, 67.80; % H, 4.38; % S,13.92. Found % C,66.45; % H, 4.50; % S,14.10; H^1 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); C^{13} 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), 10822(m). UV λ max 333(0.674), 302(1.693), 251(1.355) 210(2.459) at 0.0005M conc.

The three coupling reactions were carried out using the same general procedure. Below is the general procedure with analytical data for the other two coupled benzophenones also given.

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

A mixture of anhydrous THF (10 mL), anhydrous CH_2Cl_2 (150 mL), and 2.23 g (0.011 mole) 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 mole) of methylenebis(mercaptoacetic acid) in 50 mL anhydrous THF was added

dropwise to the stirring mixture over 1 h. The reaction mixture was allowed to warm to rt and a solution of 25 mL anhydrous THF, 25 mL anhydrous CH_2Cl_2, and 4.28 g (0.020 mole) of 2,4-dihydroxybenzophenone was added dropwise and with stirring over 1 h. The reaction was stirred at rt for 24 h and was then rotary evaporated to leave a yellow oil. This oil was dissolved in 100 mL of CH_2Cl_2 and washed with water (2x100 mL), dried over Na_2SO_4, and filtered. The filtrate gave three spots to 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 2.22g (37% yield) of the desired linked benzophenone-bissulfide, mp. 127-2°C. Calcd. % C, 63.25; % H, 4.11; % S, 10.89; Found % C, 63.15; % H, 4.15; % S, 10.98 H^1 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); C^{13} 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 0.0005M conc.

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

White crystals, 2.24 g (37% yield), mp 131-33°C; Calcd. % C, 63.77; % H, 4.49; % S, 10.64, Found % C, 63.68; % H, 4.43; % S, 10.67; H^1 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); C^{13} 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 conc.

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

White crystals, 1.80 g (31.9% yield), mp 88-89.5°C.; Calcd. % C, 63.77; % H, 4.35; % S, 10.64, Found % C, 63.66; % H, 4.32; % S, 10.59; H^1 NMR:12.41(s,2H); 7.55(m,12H), 6.77(s, 2H), 6.58(d, 8 Hz, 2H), 3.02(t, 4 Hz, 2H), 2.93(t, J = 4 Hz, 2H); C^{13} 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).

(8) 2-Hydroxy-4-(4-mercaptobutoxy)benzophenone

A solution of 150 mL of THF, 20 mL of water, 1.68g of potassium hydroxide, and 2,4-dihydroxybenzophenone 6.427g (0.030 mole) was stirred under argon for 1 h. Next, 1,4 dibromobutane was added all at once, and the reaction mixture was refluxed for 24 h. The reaction mixture was rotary evaporated to an oily mixture. This mixture was dissolved in CH_2Cl_2, and filtered. The organic layer was saved

and dried over $MgSO_4$. 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 x 12 cm) with 100% CH_2Cl_2. The first 500 mL were discarded, and the next 1 L was collected and reduced under vacuum to leave a white yellow solid, mp. 70-72°C. This solid was chromatographed again on a 4 cm x 25 cm column with CH_2Cl_2/Hexane (50/50) as the eluent to yield 3.44g of the desired 2-hydroxy-4-(4-bromobutoxy)benzophenone, mp. 81-82°C(lit.[20] mp 87°C). This solid was dissolved in methanol, cooled to 10°C, and an aqueous solution (30mL) of 0.1 M trithiocarbonate (NaSC(S)SNa) was added at one time to the cold methanolic reaction mixture. The mixture was allowed to warm to rt 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/CS_2 was removed under vacuum at rt. The aqueous phase was extracted with ethyl ether (3 x 150 mL), and the ether extracts were dried over $MgSO_4$. 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 CH_2Cl_2/hexane on a silica gel column (4 cm x 25 cm). An off-white solid,1.84 g, mp 68-72°C, was obtained, which proved to be the desired compound. The compound appeared to be completely pure to GC, but titration with Ellman's reagent indicated that the solid was 92.5% thiol with the rest being the disulfide. H^1 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); C^{13} 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.

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

This compound proved to be impossible to synthesize using the modified EDC procedure, so a literature [21] procedure for the mild reduction of alkyl sulfides was used. A dioxane/water solution (50/50, 150 mL) was purged with argon for 4 h. To this solution, previously synthesized **7** (1.50 g, 0.0025 mole), 0.05 g of EDTA, 0.1 g of NaCl, and 7.5 mL of 0.1 N HCl were added at one time. Next, 1.31 g (0.005 mole) of triphenylphosphine were added, and the reaction was warmed to 40°C for 2 h and then cooled to rt. The reaction was poured into 100 mL of ethyl ether/100 mL water, and the organic layer was saved. The organic phase was washed with water (100 mL), dried over $MgSO_4$, 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 x 25 cm column using silica gel and CH_2Cl_2/hexane (30/70) as the eluent. White waxy crystals (1.23g), mp 37-40°C, were obtained. Calcd. % C, 63.56; % H, 4.67; % S, 10.60; Found % C, 63.58; % H, 4.66; % S, 10.50. H^1 NMR:12.30 (s, 2H), 7.52 (m, 12H), 6.77 (s, 2H), 6.60 (d, J =2.4Hz, 2H), 2.82 (m, 4H), 1.65 (t, J = 8.0 Hz, 3H); C^{13} 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 conc.

(10) 2-Hydroxy-4-propionylbenzophenone

An anhydrous THF solution (150 mL), potassium carbonate (0.57 g), and 2,4-dihydroxybenzophenone (4.28 g, 0.020 mole) solution were stirred under argon for 1 h. Next, propionyl chloride (2.00g, 0.020 mole) was added all at once, 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 x 24 cm silica gel column with hexane/CH_2Cl_2 (50/50) as the eluent. Fractions 10-21 (25 mL) were collected and combined to yield 4.46 g of desired product as an oil, which proved to be 98.7% pure by GC. H^1 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); C^{13} 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 conc.

3. Discussion

During our initial investigation directed at optimizing the use of additive mixtures for mechanical pulp, we explored the mechanisms contributing to the observed synergistic effects. The principle photostabilization mechanism of most benzophenone derivatives is absorption of near-UV light and then dissipation of this energy in a manner that does not lead to photosensitization. The light stability of these UV-absorbers is attributed to fast non-radiative decay mechanisms from the excited state to the ground state, which has been shown to be due to the internal hydrogen bond between the two-hydroxy group 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 as radical scavenger agents in a manner reminiscent of the pathways described in Figure 2 [22]. The synergistic effects noted with thiol additives and benzophenone derivatives in mechanical pulp could 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 onto BCTMP test sheets, including 2-hydroxy-4-methoxybenzophenone **(1)**, 2,4-dihydroxybenzophenone **(2),** and 2-hydroxybenzophenone **(3)**. The results of photolyzing the BCTMP and cellulose test sheets are summarized in Table 1.

After irradiation, each testsheet was soxhlet extracted, and the extracts were spectroscopically characterized. In each case, product analysis of the extracts indicated that only starting material was present, and yields were greater than 99% for the first two hours of irradiation on BCTMP test sheets. After irradiation for 8 h, all three benzophenone derivatives were recovered from the BCTMP in greater than 90% yield with benzophenone **3** affording the lowest recovery yield of 92.6%. Upon 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 most likely 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] that methyl-3-hydroxy-4-benzoylphenoxyacetate impregnated on mechanical pulp was relatively stable upon irradiation.

Control experiments using cellulose as a support matrix indicate that the three benzophenones do 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 mostly due to post-photolysis reactions involving reactive lignin fragments. In summary, these results suggest 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. Studies highlighted in this report suggest that the degradation of benzophenone derivatives during photolysis of mechanical pulp is a slow process and certainly does not play a dominant role in the early phase of photoaging. In turn, these results suggest 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 that suggest that the phenols should scavenge thiyl radicals [24] and hence would not regenerate the benzophenone radical.

To determine if there were any beneficial effects to having the radical scavenger in close association with the UV absorber, we synthesized a series of novel benzophenone derivatives that incorporated 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 incorporating either a thiol group, a bismethylene disulfide [$RSCH_2SR$], a bisethylene disulfide [$RSCH_2CH_2SR$], or a disulfide group, each attached to the 4 position of benzophenone. Each of these sulfur functional groups has been previously shown to be an effective photostabilization agent for mechanical pulp. Figure 3 summarizes the synthetic methodology employed for these studies.

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 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 distribution 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 sheets basis; [c]photostabilization effect = [(change in brightness for treated testsheet) - (change in brightness for untreated testsheet)]/(change in brightness for untreated testsheet) %; brightness changes are monitored by measuring the % reflectance light centered at 457 nm following standard methods; [d] %benzophenone recoveries were determined by extended soxhlet extraction and characterizing the extracts by GC/MS, ^{1}H NMR, and TLC, in all cases, only starting material was detected in the extracts.

Our initial synthetic target was to prepare the 4-thiol derivative of 2,4-dihydroxybenzophenone, which was readily prepared by treating **2** with dimethylthiocarbamoyl 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 had 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 1-(3-dimethylaminopropyl)-3-ethylcarbodiimidehydrochloride (EDC) and the appropriate diacid as shown in Fig. 3.

The brightness stabilization properties of the benzophenone derivatives **5-7** were compared to the photostabilization properties of 4-alkyl substituted benzophenone derivatives (**1** & **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 further than benzophenone additives **1** and **9**. These results suggest that the attachment of the sulfur group to the benzophenone unit was not beneficial. This conclusion was further confirmed by treating test sheets of BCTMP with molar equivalents of the benzophenone **1**, dimethyl esters of **11** or **12**, benzophenones **5-8**, or combinations of benzophenone **1** and the dimethyl esters of **11** or **12**. The resulting BCTMP test sheets were photolyzed, and at selected time periods the % reflectance values for the irradiated test sheets were recorded. Figure 5 summarizes the results of these photolysis studies, and in each case, the unlinked additive mixture provided 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 effects occurred when the benzophenone and mercapto additives were added as separate compounds to the BCTMP testsheet, as shown in Fig. 6. Previous studies by Pan et al. [12] had demonstrated that the use of additive mixtures provides a distinct advantage at retarding the overall rates of brightness reversion.

A comparison of the UV absorbance of 2,4-dihydroxybenzophenone (**3**) (UV max 322 nm), 2-hydroxy-4-methoxybenzophenone (**1**) (UV max 323 nm), 2-hydroxy-4-propionylbenzophenone (**10**) (UV λmax 326 nm), and 2-hydroxy-4-(4-mercapyobutoxy)benzophenone (**8**) (UV λmax 314 nm) shows little difference in absorbance in the 300-400 range (all had approximately the same absolute absorbance in this range). Therefore, the differences in photostabilization between linked and unlinked additive mixtures were 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 as compared to the unlinked additives. The results of these investigations suggest that there is no intrinsic benefit to having the sulfur-based antioxidant closely associated with the UV absorber absorbed on the BCTMP pulp fiber.

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 observed between thiol and benzophenones for 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 benzophenone derivatives reducing the overall flux of light transmitted onto the pulp 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 the 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 is by employing several additives that operate on differing components of the overall brightness reversion phenomenon.

Acknowledgments

This investigation was made possible by the financial support provided by the National Science Foundation (Grant CTS-9414695).

References

1. Cockram, R.A.; Proceedings of the 1989 International Mechanical Pulping Conference, Helsinki, June (1989).

2. Heitner, C.; in Photochemistry of Lignocellulosic Materials, Heitner, C. and Scaiano, J.C., eds., ACS Symposium Series 531, Washington D.C., 8, 1993.

3. Leary, G.J.; J. Pulp Paper Sci., 20(6):j154 (1994).

4. a) Zhang, L.; Gellerstedt.; Proceedings of the 7th International Symposium on Wood and Pulping Chemistry; Beijing, China, Volume 2, (1993), 759-66.

   b) Castellan, A.; Nourmamode, A.; Jaeger, C.; Nordic Pulp Paper Res., 8(2), (1993), 239.

   c) Forsskahl, I.; Tylli, H.; Olkkoner, C.; Proceedings of the 7th International Symposium on Wood and Pulping Chemistry, Beijing, China, Volume 2, (1993), 750.

   d) Jaeger, C.; Nourmamode, A.; Castellan, A., Holzforschung, 47, (1993), 375.

5. Vanucci, C.; Fornier de Violet, P.; Bovas-Laurent, H.; Castellan, A.; J. Photochem. Photobiol., A: Chemistry, 41 (1988), 251.

6. a) Gratzl, J.S.; Das Papier, 39(10A), V14, 1985.

   b) Berinstain, A.B.; Whittelsey, M.K.; Scaiano, J.C.; in Photochemistry of Lignocellulosic Materials, Heitner, C. and Scaiano, J.C., eds., ACS Symposium Series 531, Washington D.C., 8, 1993, 111.

   c) Hon, D.N.-S.; J. Wood Chem. Technol., 12(2), (1992), 179.

7. Schmidt, J.A.; Heitner, C.; J. Wood Chem. Technol., 13(3), (1993), 309.

8. Schmidt, J.A.; Heitner, C.; J. Wood Chem. Technol., 11(1), (1991), 397.

9. Cole, B.J.W.; Sarkanen, K.V.; Tappi J., 70(11):117 (1987).

10. Francis, R.C.; Dence, C.W.; Alexander, T.C.; U.S. Patent 5,080,754, (1992).

11. Davidson, R.S.; Dunn, L.A.; Castellan, A.; Colombo, A.; Nourmamode, A.; Zhu, J.H.; J. Wood Chem. Technol., 11, (1991), 419.

12. Pan, X.; Harvey, L.C.; Ragauskas, A.J.; J. Pulp Paper Sci., 22(4), (1996), J135-J140.

13. a) Ciba-Geigy: Tinuvin 1130, Publication no. 285481e, 1987.

   b) Hodgeman, D.K.; Bellart, E.P.; J. Polymer Sci.: Polymer Chem. 18, (1980), 1105.

14. Davidson, R.S.; Dunn, L.; Castellan, A.; Nourmamode, A.; J. Photochem. Photobiology A: Chemistry, 86 (1995), 275.

15. Wan, J.K.S.; Tse, M.Y.; Heitner, C.J.; J. Wood Chem. Technol., 13(4), (1991), 327.

16. Tappi Procedures T-205 and T-218, Tappi Test Methods 1991, Tappi Press, Atlanta, GA, (1990).

17. Tappi Procedures T-452 and T-534, Tappi Test Methods 1991, Tappi Press, Atlanta, GA, (1990).

18. Method taken from Newman, M.S.; Hetzel, F.W., Org. Synth., 51, (1971), 139.

19. Grassetti, D.R.; Murray, J.F., Jr.; Arch. Biochem. Biophys., 119, (1967), 41.

20. Castellan, A.; Noutary, C.; Davidson, R.S.; J. Photochem. Photobiology A: Chemistry, 84 (1994), 311.

21. Method taken form Overman, L.E.; O'Conner, E.M.; J. Am. Chem. Soc., 98:3 (1976), 771-775.

22. Gugumus, F.; Polymer Degrad. and Stabil., 39, (1993), 117.

23. Trichet, V.; Grelier, S.; Castellan, A.; Choudhury, H.; Davidson, R.S.; J. Photochem. Photobiology A: Chemistry, 95 (1996), 181.

24. Scott, G.; in "Atmospheric Oxidation and Anti-Oxidants," Scott, G. ed., Elsevier, London, (1993), 284-90.

25. McMillen, D.F.: Golden, D.M.; Ann. Rev. Phys. Chem. 33, 493(1982).

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

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

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

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

Fig 5: Comparative photoyellowing properties of BCTMP hardwood pulp test sheets treated with benzophenone derivatives **1**, **5**, **6**, **9,** and (**1+11, 1+12**).

Fig 6. Comparative photoyellowing properties of BCTMP hardwood pulp test sheets treated with benzophenone derivatives **1**, **8**, **9,** and (**1**+$HOCH_2CH_2SH$).

Figure 1

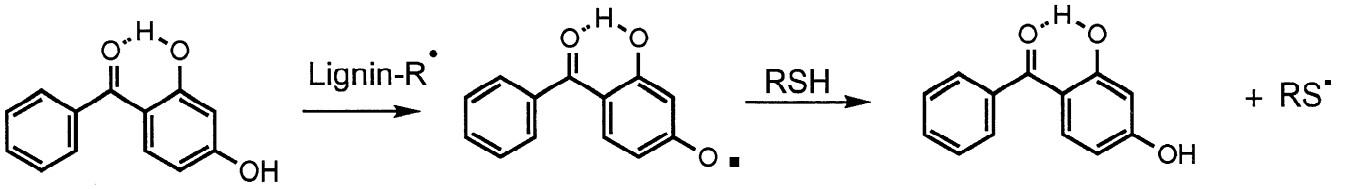
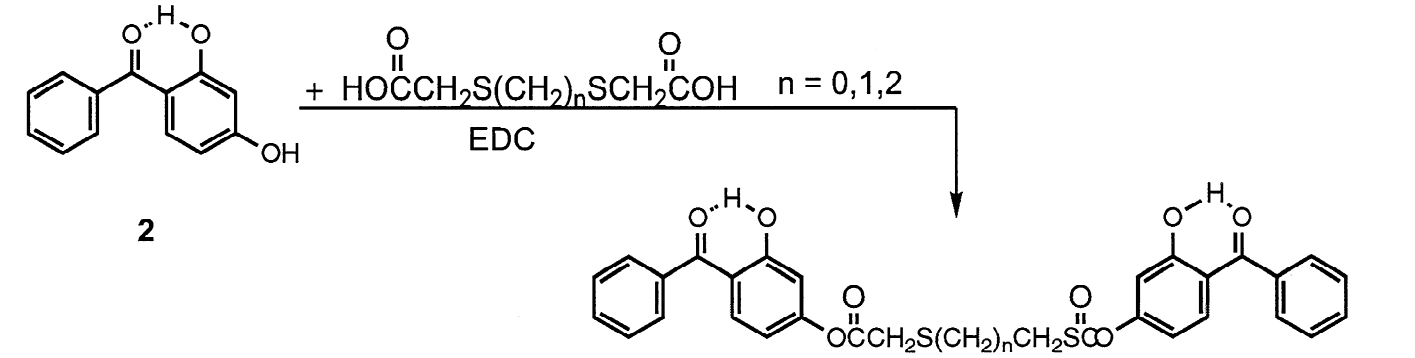
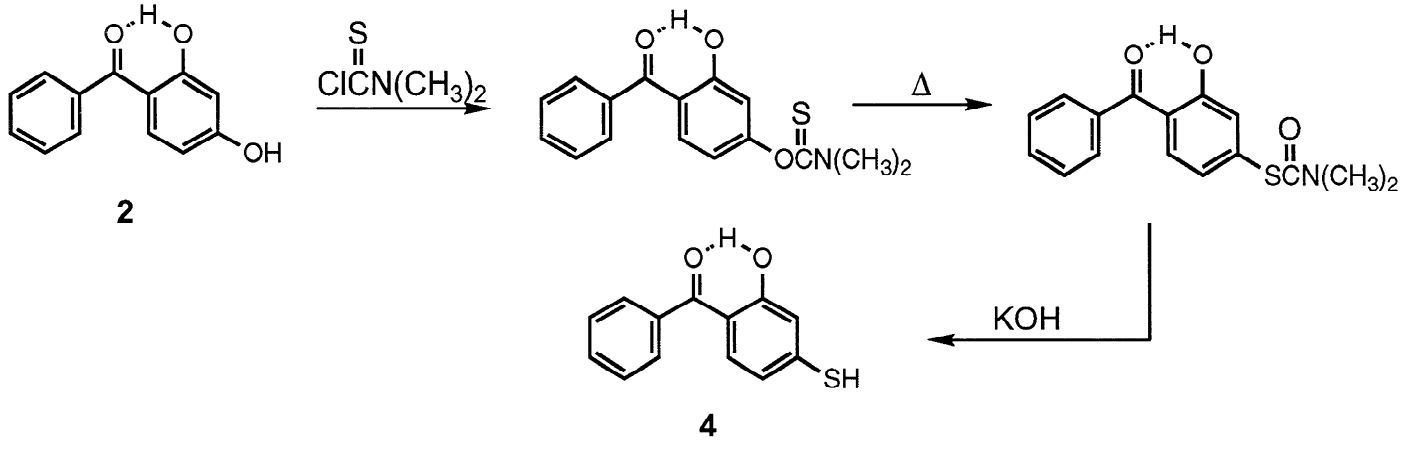


Figure 2





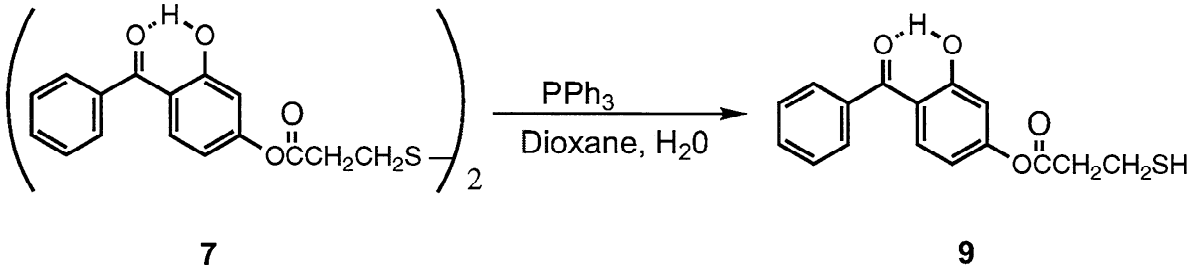


Figure 3

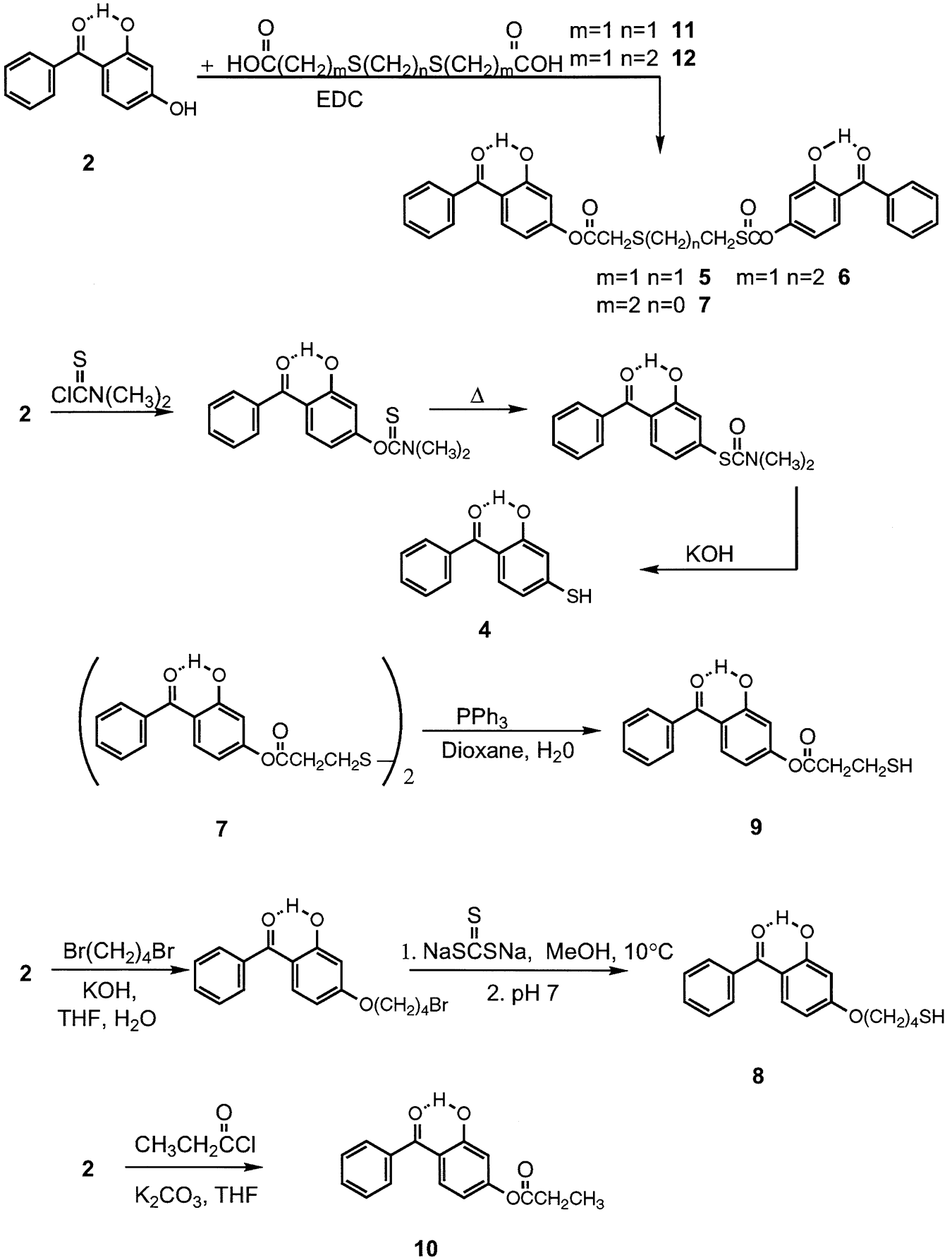

+ HOC(CH2)mS(CH2)nS(CH2)mCOH
m=1 n=1 11
m=1 n=2 12
EDC
2
m=1 n=1 5
m=1 n=2 6
m=2 n=0 7
ClCN(CH3)2
Δ
KOH
4
PPh3
Dioxane, H20
7
9
Br(CH2)4Br
KOH,
THF, H2O
1. NaSCSNa, MeOH, 10°C
2. pH 7
8
CH3CH2COCl
K2CO3, THF
10

Figure 4

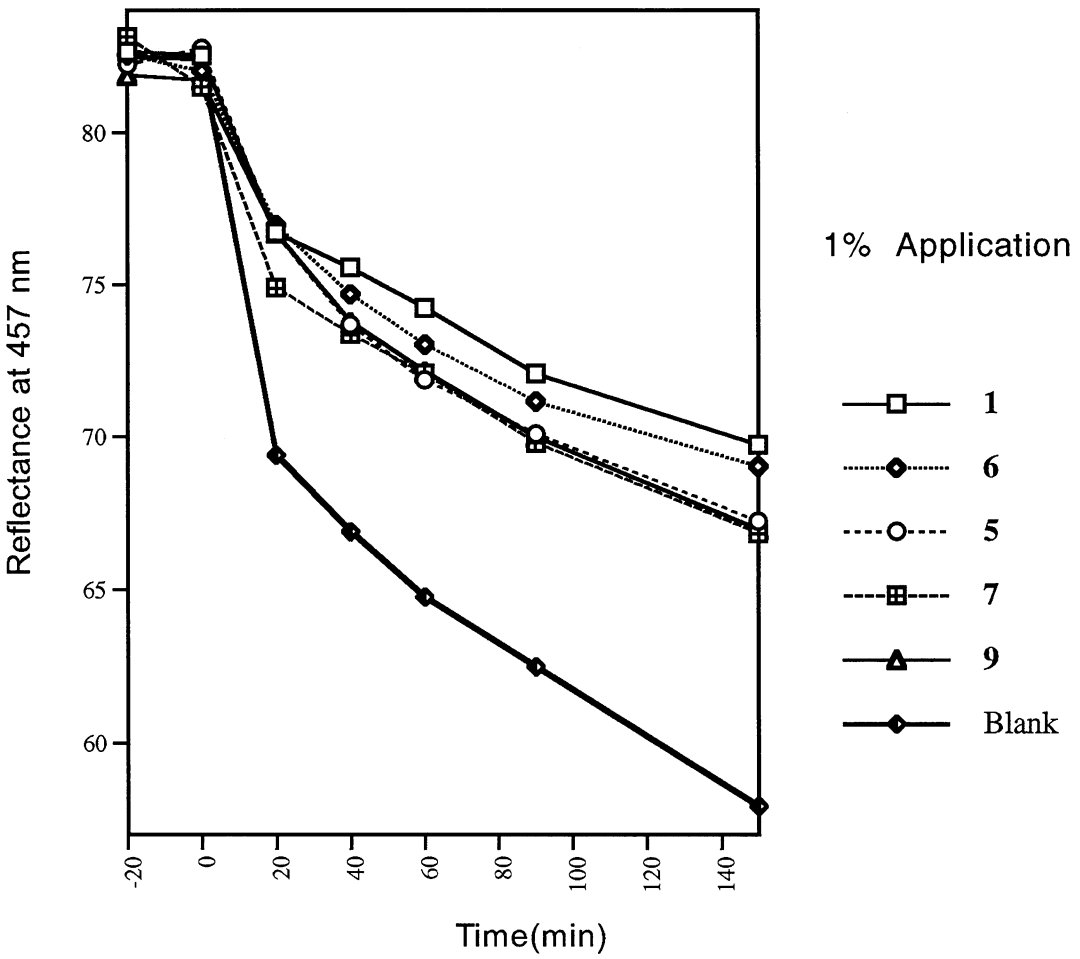

Reflectance at 457 nm
80
75
70
65
60
-20
0
20
40
60
80
100
120
140
Time(min)
1% Application
1
6
5
7
9
Blank

Figure 5a

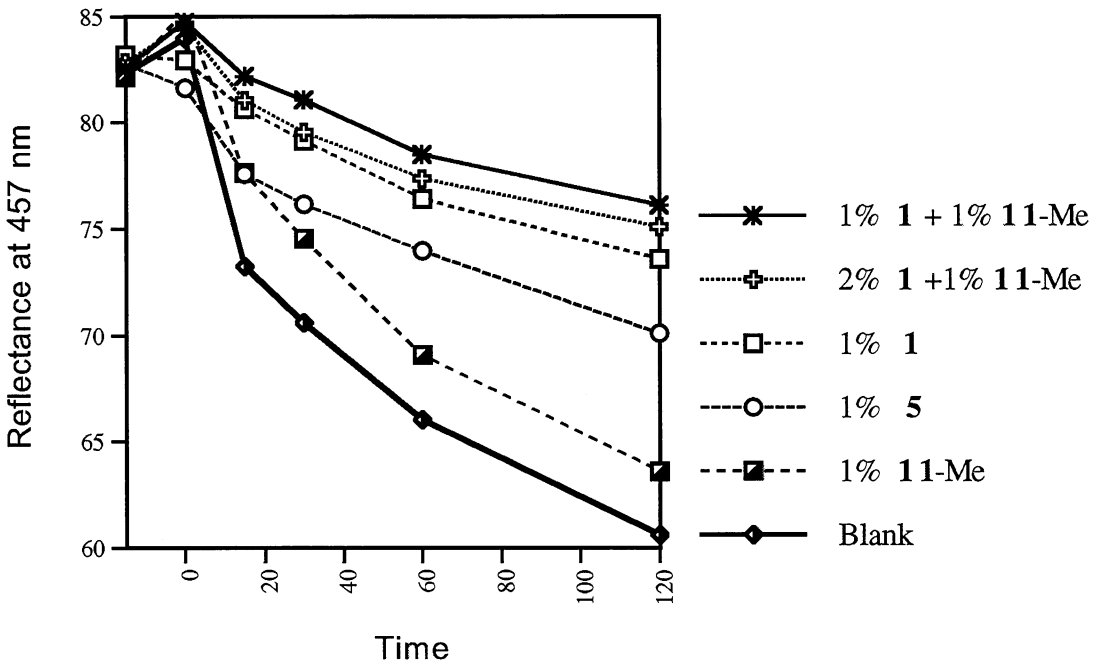

Reflectance at 457 nm
85
80
75
70
65
60
0
20
40
60
80
100
120
Time
1% 1 + 1% 11-Me
2% 1 +1% 11-Me
1% 1
1% 5
1% 11-Me
Blank

Figure 5b

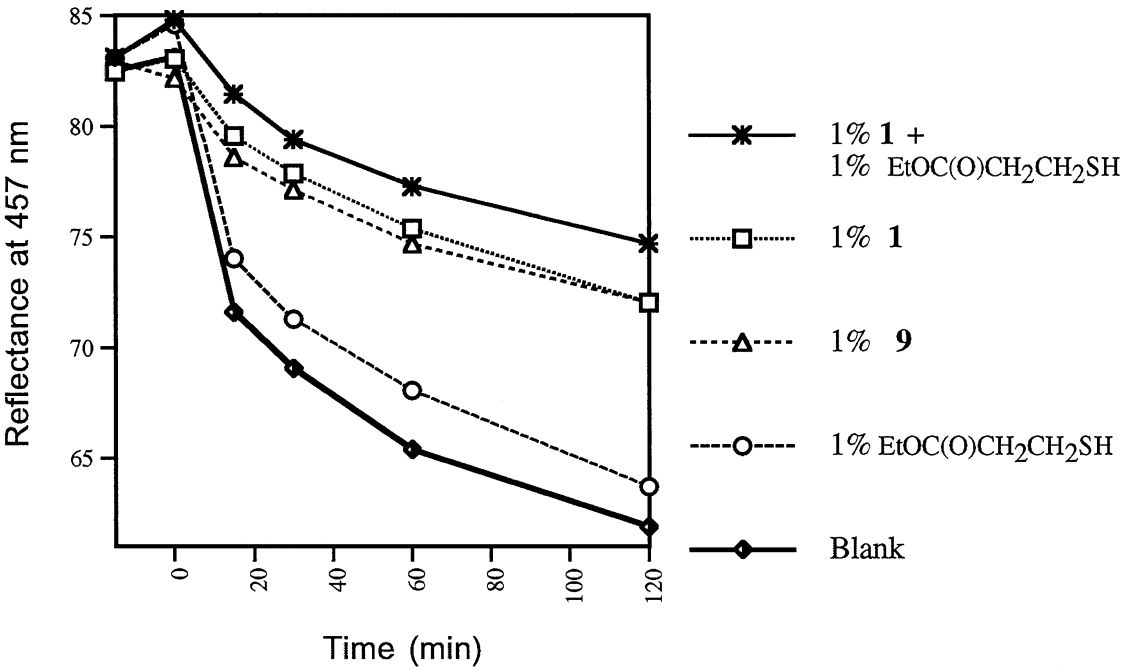
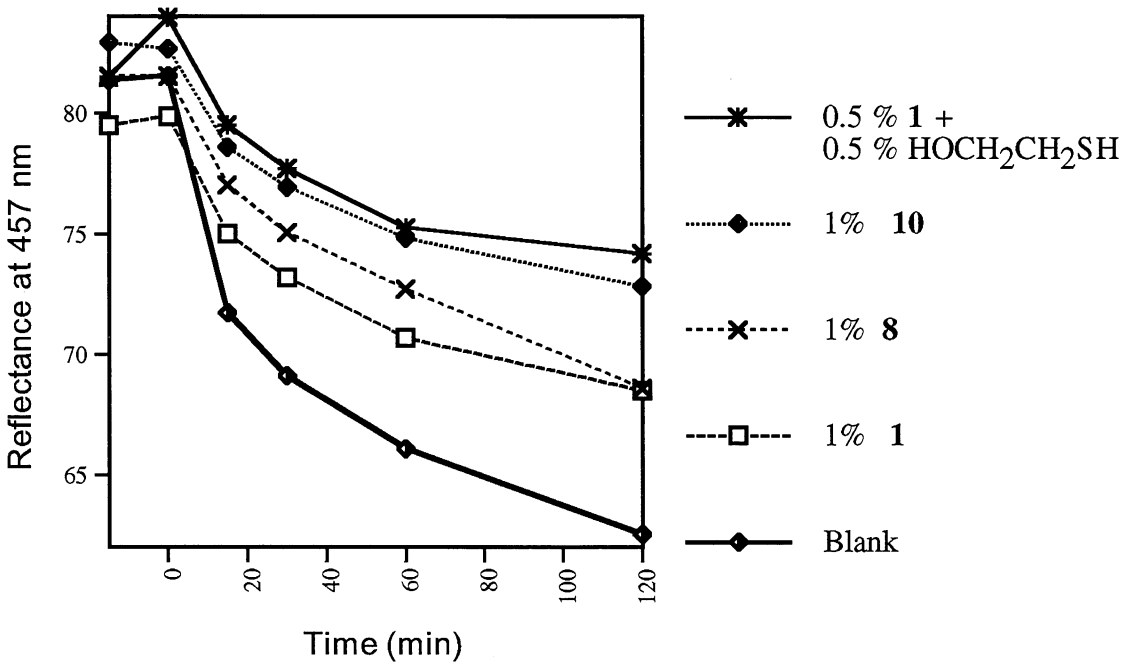

Reflectance at 457 nm
85
80
75
70
65
0
20
40
60
80
100
120
Time (min)
1% 1 +
1% EtOC(O)CH2CH2SH
1% 1
1% 9
1% EtOC(O)CH2CH2SH
Blank

Figure 6


Reflectance at 457 nm
80
75
70
65
0
20
40
60
80
100
120
Time (min)
0.5 % 1 +
0.5 % HOCH2CH2SH
1% 10
1% 8
1% 1
Blank