

# Photostabilization of Bagasse Chemimechanical Pulp through Acetylation in Liquid Phase

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Received: 28 February 2005; accepted: 27 June 2005

## ABSTRACT

Papers made from bagasse chemimechanical pulp were chemically modified by acetylation. A combination of sodium borohydride reduction and acetylation was also tested. Efficient inhibition of photo-yellowing of papers made from bagasse CMP was achieved by acetylation. The acetylated unbleached CMP was noticeably photo-bleached during irradiation. Sodium borohydride reduction followed by acetylation had the same effect as acetylation alone at the same degree of reaction time. The pre-reduced, acetylated unbleached papers were, however, not brightened during irradiation. The reductive treatment had little effect in reducing the photo-yellowing of paper made from CMP pulp; a small stabilization effect was observed in the case of bleached CMP, while unbleached CMP was slightly more prone to discolor in the later phase of photo-reversion. The improved stability towards light was closely related to the decrease in the phenolic hydroxyl content as a result of blocking by acetyl groups during treatment with acetic anhydride. The results support the hypothesis that phenolic hydroxyl has an important role in the process of photo-reversion of high-yield pulps.

### Key Words:

acetylation;  
photo-discolouration;  
brightness;  
chemimechanical pulp;  
sodium borohydride;  
bagasse.

## INTRODUCTION

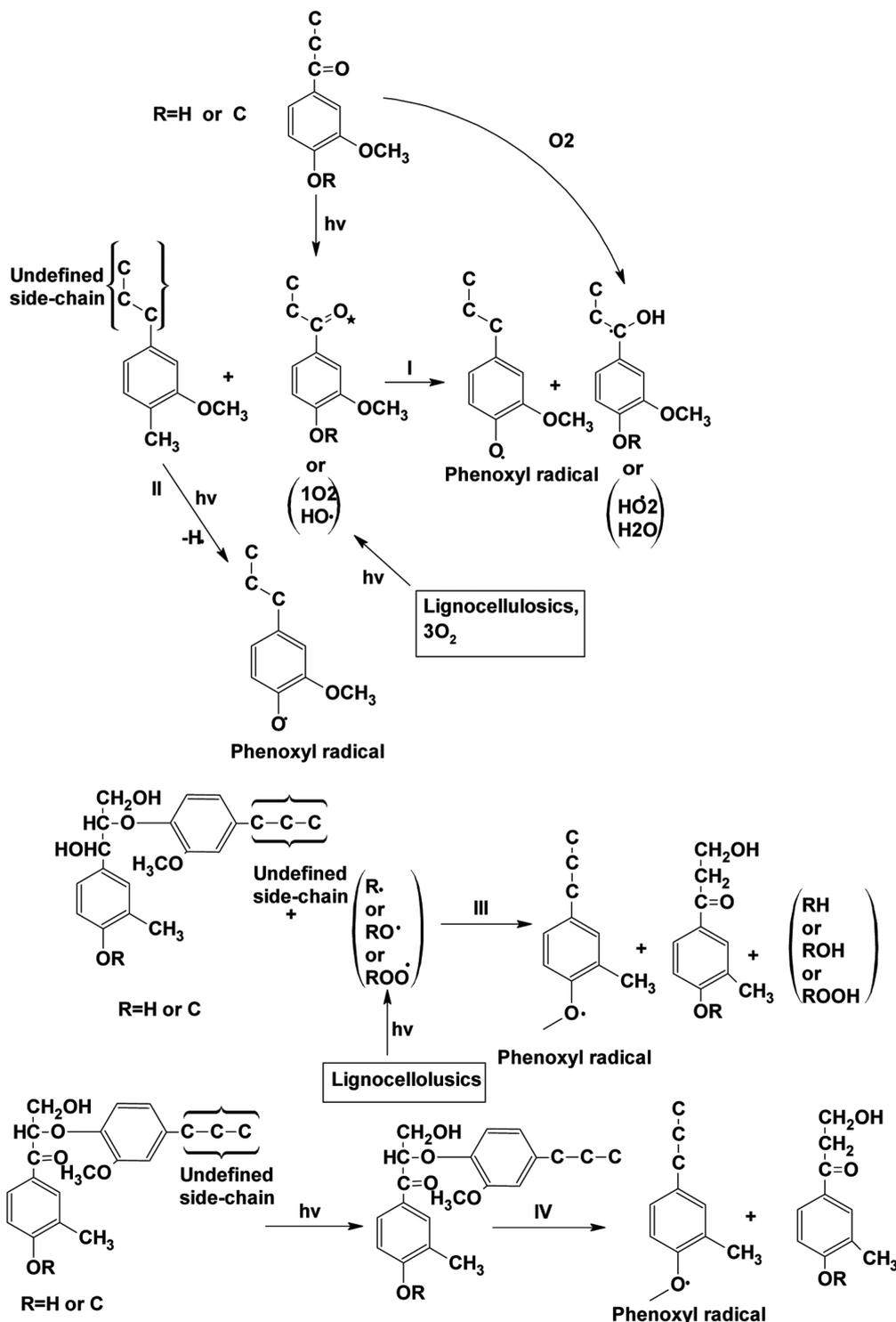
There is a great potential in using mechanical pulps in high value applications. Today, lignin-rich pulps are primarily used in low-value and short-life products such as newsprint, catalogue papers and magazine papers. The major draw-

back that prevents a more widespread utilization of high-yield pulps in high quality printing papers is the difficulty in maintaining their bleached brightness over the product lifetime. The insufficient brightness stability is due to a rapid light-

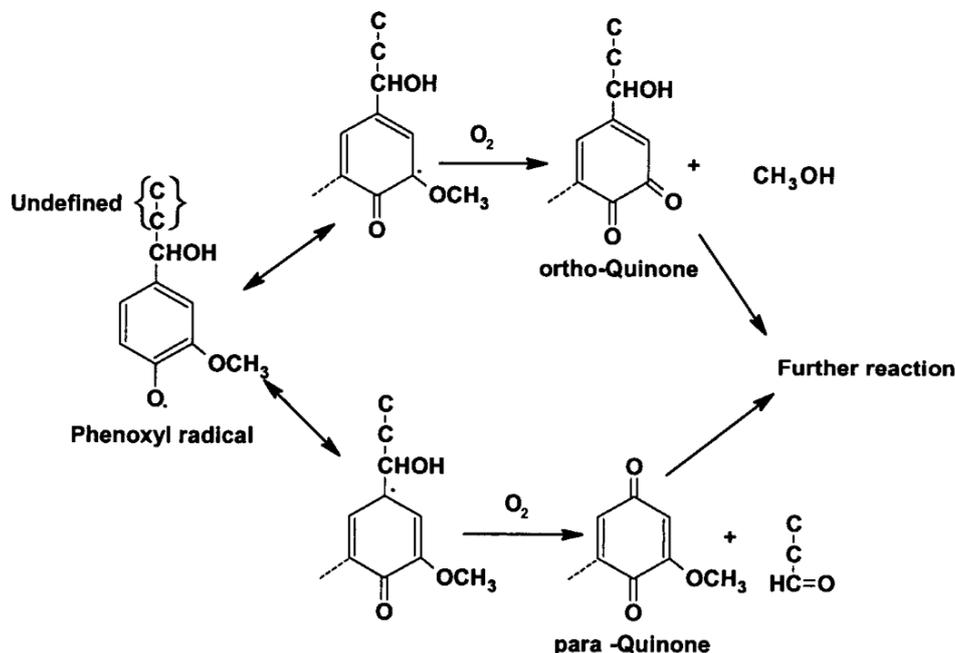
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induced oxidation (i.e., yellowing) when such papers are exposed to daylight. Over the last decades, extensive research has been conducted to elucidate the

mechanisms of yellowing which is a necessity if methods are to be found for preventing or at least retarding photo-yellowing. Schemes I and II show the proposed



**Scheme I.** Proposed reaction pathways (I-IV) in the formation of radicals during photo-yellowing (based on the mechanism given in Paulsson 2002) [1].



**Scheme II.** Proposed reaction pathways in the formation of ortho- and *para*-quinones from phenoxyl radicals during photo-yellowing (based on the mechanism given in Paulsson 2002) [1].

reaction pathways for the formation of radicals (phenoxyl, ketyl, etc.) and those for the formation of chromophores (initially quinones), respectively [1]. Although many questions still remain, it is generally accepted that the photo-oxidation of lignin in the presence of oxygen is the main cause of yellowing [2]. The lignin photo-degradation process is initiated by the absorption of ultraviolet radiation of wavelength between 290 and 400 nm [3]. Aromatic ketones ( $\alpha$ -carbonyl groups) and ring-conjugated double bonds together with phenolic and  $\alpha$ -hydroxyl groups are the essential functional groups in the suggested reaction sequences leading to discolouration. Important intermediates in the photo-yellowing process are phenoxyl free-radicals, which are oxidized in the presence of ground-state oxygen into chromophoric structures of the quinonoid type [4]. The discolouration reactions involve complex and inter-related pathways for the formation of phenoxyl free-radicals. At least three general reaction routes for the formation of phenoxyl radicals have been suggested. One involves the direct abstraction of phenolic hydroxyl hydrogen by  $\alpha$ -carbonyl groups in the triplet excited state, singlet oxygen or hydroxyl radicals [5]. Photochemical cleavage of  $\beta$ -aryl ether linkages adjacent to be considered being

another significant contributor to phenoxyl radical formation [6, 7]. The photo-induced yellowing has also been attributed to the photoreactivity of phenolic chromophores absorbing ultraviolet radiation above 300 nm and giving phenoxyl radicals by direct photolysis mechanism without any need to photo-sensitizers [8, 9].

Chemical modification of potential chromophoric groups has been examined [10-15]. The removal of photosensitive carbonyl groups by reduction was shown to have a limited effect in protecting lignin against photo-degradation. Derivatization of hydroxyl groups by alkylation or acylation has been more successful. Acetylation of ground wood pulps improved the resistance towards light and, in some cases, also photobleached the pulp [11, 16, 17]. Acetylation can also inactivate or remove some chromophores initially present in unbleached or dithionite bleached pulps. Methylation in the presence of a cationic phase transfer catalyst was reported to reduce the yellowing rate significantly in the case of hydrogen peroxide bleached CTMP [15]. The improved photostability observed for acetylated or methylated pulps was, however, accompanied by a substantial decrease in strength. A previous investigation has shown that the acetylation of paper made from spruce TMP and aspen CTMP rapidly

removes phenolic hydroxyl groups, and that the paper strength properties are remained almost unaltered in the dry state but considerably increase in the wet state [18]. It was therefore of interest to examine how the photostabilization of papers made from bagasse (as a non-wood resource of fibres) CMP pulp was affected by different degrees of acetylation. The effect of sodium borohydride reduction alone or in combination with acetylation is also reported in the present paper.

## Experimental

### Materials

Depithed bagasse, obtained from Pars Pulp and Paper mill. The chemimechanical pulp was prepared by chemical pre-treatment of bagasse with sodium sulphite (8%) and sodium hydroxide (4%) for 20 min in 95°C. After chemical treatment the stuff was refined by a laboratory single disc refiner under atmospheric conditions to reach a freeness level of 350 mLCSF according to T 227 om-99 Tappi standard method. All the chemical materials used in the experiments were obtained from Merck as laboratory grade and were used as received. Deionized water was used in all the experiments.

### Hydrogen Peroxide Bleaching

CMP pulp was bleached with hydrogen peroxide according to the method proposed by Ni et al. [19] under following conditions: Hydrogen peroxide 5%, sodium hydroxide on hydrogen peroxide ratio 0.8, DTPA (diethylene triamine pentaacetic acid) charge 0.5%,  $MgSO_4$ : 0.05%,  $Na_2SiO_3$ : 3%, pulp consistency: 18%, time: 2 h, temperature: 65°C.

### Sodium Borohydride Reduction

#### *Hydrogen Peroxide Bleached Pulp*

The procedure applied was according the method specified by Ek et al. [17], with some modifications. Hydrogen peroxide bleached bagasse CMP pulp (1% consistency) and EDTA (ethylene diamine triacetic acid) (0.15% consistency) were suspended in water and stirred for 1 h at room temperature, after which it was washed and filtered. The pulp was then suspended in water (1% consistency) and sodium borohydride was added (5% on pulp weight basis). The pulp suspension

was stirred at room temperature for 3 days, followed by filtering, washing with water and air-drying at room temperature.

#### *Reduction of Unbleached Pulp*

Reduction of unbleached pulp was performed as following: unbleached pulp samples (5 g, 1% consistency) and DTPA (0.5 g, 0.5% consistency) were suspended in water (500 mL) followed by a water wash and filtration. These pulp samples were then suspended in water (100 mL) containing 2.5 g sodium borohydride. The suspension was stirred at room temperature for 3 h, after which the pulp was carefully washed and air dried.

### Lignin Content

The lignin content, determined as Klason lignin and acid-soluble lignin, was 18% for the unbleached pulp and 17.8% for bleached bagasse CMP pulp. The acid-soluble lignin was measured spectrophotometrically at 205 nm.

### Handsheet Preparation

Handsheets (60 g.m<sup>-2</sup>) were prepared according to TAPPI T205 om-88. The paper sheets were then conditioned for 24 h at 23°C and 50% rh according to TAPPI T205 om-88 before acetylation.

### Acetylation

The paper sheets were acetylated using a technical grade of acetic anhydride (liquid phase, without any catalyst, 80 and 100°C) for 10, 25, 60 and 120 min to obtain different degrees of acetylation. The procedure was as follow:

Conditioned handsheets were placed in a preheated flask with an excess of acetic anhydride. After the reaction time was completed, the handsheets were immersed in water to stop the acetylation reaction. The acetylated paper were then thoroughly washed with water to remove remaining chemicals and thereafter pressed for 5 min at 400 kPa. The sheets were dried on the press plates (24 h) and then conditioned at 23°C and 50% rh according to TAPPI T205 om-88 before analysis. In order to study the effect of pulp acetylation and comparing the results with those of acetylated handsheets, CMP pulp was also acetylated using the same procedure.

### Accelerated Photo-aging

The irradiation procedure was the same as that described by Gellerstedt et al. [20]. Handsheets were fastened onto a vertical fibre-glass cylinder rotating at 2 rpm. The cylinder was surrounded by 12 vertical fluorescent tubes (6 Tungsram 20W-F74 and 6 Philips F20W/ 350 BL) placed symmetrically inside an outer cylinder made of fiber-glass. The combination of fluorescent tubes was chosen to simulate sunlight, i.e. both UV and visible irradiation. The distance between the paper cylinder and the light-tubes was 6 cm. The temperature was kept close to room temperature with 3 fans placed in top and bottom of the cylinder.

### Optical Properties

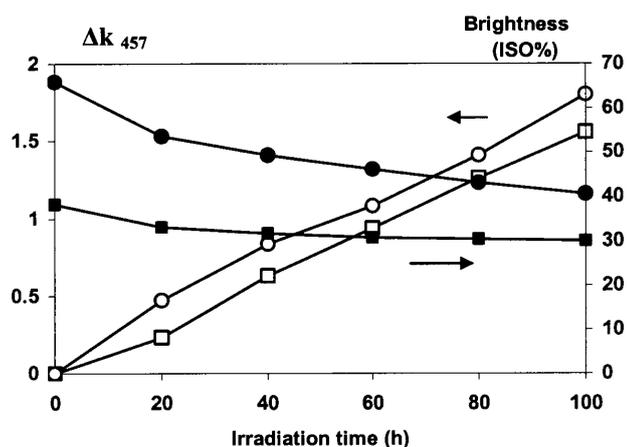
Specific light absorption ( $k$ , 557 nm) and light scattering ( $s$ , 557 nm) coefficients were calculated using the Kubelka-Munk theory. The degree of brightness reversion during irradiation was expressed as the Post Color (PC) number (at 457nm). The Kubelka-Munk equation was used to calculate  $k \cdot s^{-1}$  according to Giertz [21]:

$$(k \cdot s^{-1}) = [(1 - R_{\infty})^2 \cdot (2 R_{\infty})^{-1}]$$

Where  $R_{\infty}$  = reflectance of an optically thick sheet. Then, the PC- number was then calculated according to:

$$PC = 100[(k \cdot s^{-1})_t - (k \cdot s^{-1})_{t=0}]$$

Where  $t$  = irradiation time,  $k$  = light absorption coefficient and  $s$  = light scattering coefficient.



**Figure 1.** Brightness ( $R_{\infty, 457}$ , filled symbols) and the difference in light absorption coefficient ( $\Delta k_{457}$ , unfilled symbols) after long-term light-induced aging of bagasse CMP paper samples. ( $\square$ ), unbleached CMP; ( $\circ$ ) hydrogen-peroxide bleached CMP.

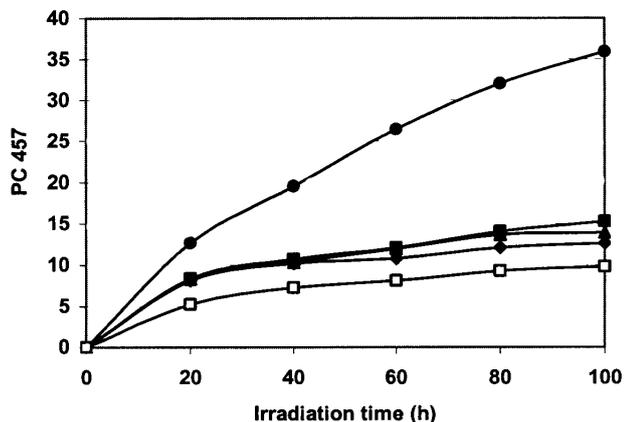
### Instruments

Brightness ( $R_{\infty}$ , 457 nm) and CIELAB colour scales ( $L^*$ ,  $a^*$ ,  $b^*$  values) were measured on 60 g.m<sup>-2</sup> paper sheets using a Technibrite Micro TB-1C spectrophotometer.

## RESULTS AND DISCUSSION

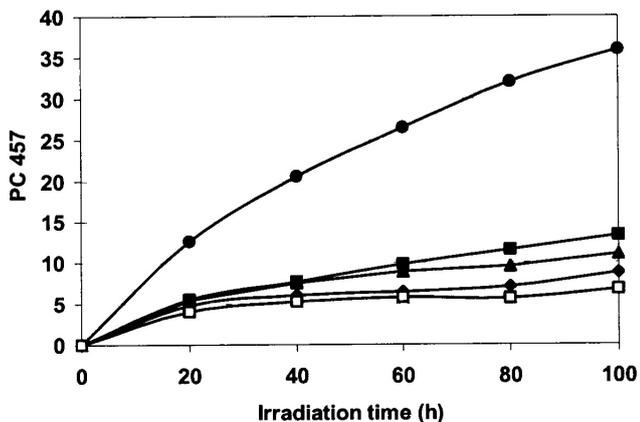
### Irradiation of Unbleached and Hydrogen-peroxide Bleached CMP Pulp

The brightness ( $R_{\infty}$ ) and change in light absorption coefficient ( $\Delta k$ ) of bagasse CMP paper samples after irradiation for up to 100 h are shown in Figure 1. The light-induced yellowing is characterized by a rapid initial phase followed by a slower phase, as reported previously [17, 22, 23]. It is also evident that the degree of yellowing is more pronounced for the hydrogen peroxide bleached CMP than for the unbleached CMP [7]. The brightness values for unbleached and bleached papers were 30% and 40%, respectively. Regarding the trend of brightness decrease of unbleached papers, it is expected that by continuing the irradiation, the final brightness of two samples end up to the same values. The yellowing evaluated accordingly to the CIELAB system, was manifested as an increase in  $b^*$  and a decrease in  $L^*$  that is equivalent to a yellower colour of paper. The changes in H<sub>2</sub>O<sub>2</sub> bleached CMP is more evident. This means that applying hydrogen peroxide could lead to formation of some light sensitive structures which can generate colored components during photo-aging. In other words, the brightness gain after bleaching is temporary. The brightening effect of hydrogen peroxide has been attributed to reactions with chromophoric structures in the lignin such as coniferaldehyde units and quinonoid structures. Pan et al. [1994] reported the major change that occurs on bleaching is a decrease in the content of coniferaldehyde structures present in the lignin [24]. It was also shown that the overall structure of the lignin was unaffected by the bleaching conditions. The partial elimination of coniferaldehyde structure by treatment with hydrogen peroxide has also been reported by other investigator [25-29]. Because of incomplete accessibility, the elimination of this structure is not possible under commercial bleaching conditions. Model compound studies have, however, shown that coniferaldehyde structures are readily cleaved by alkaline hydrogen peroxide yielding aromatic aldehydes [30].

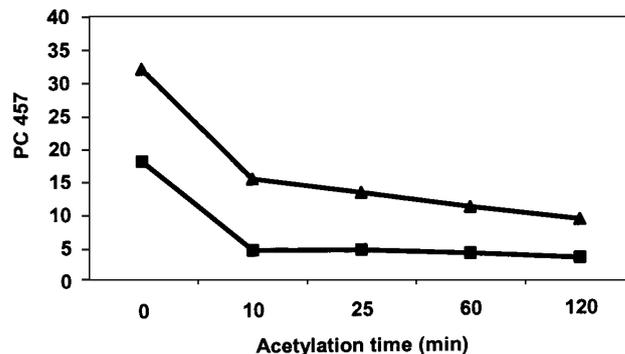


**Figure 2.** The effect of acetylation on the post colour (PC) number after accelerated long-term irradiation of unbleached and acetylated (80°C) unbleached Bagasse CMP paper samples. The numbers in brackets denote the acetylation time (min). (●), control; (■), (10); (▲), (25); (◆), (60); (□), (120).

According to Castellan et al. [1993], methoxyhydroquinones formed during hydrogen peroxide bleaching has a key role in brightness reversion of bleached mechanical pulp [31]. Furthermore, it has been shown that diguaiacylstilbenes are to a large extent responsible for the initial fast discolouration of high-yield pulps [32,33]. Briefly, stilbene, methoxyhydroquinone and coniferaldehyde units also quinonoid chromophores are present after peroxide bleaching [23].



**Figure 3.** The effect of acetylation on the post colour (PC) number after accelerated long-term irradiation of unbleached and acetylated (100°C) unbleached bagasse CMP paper samples. The numbers in brackets denote the acetylation time (min). (●), control; (■), (10); (▲), (25); (◆), (60); (□), (120).

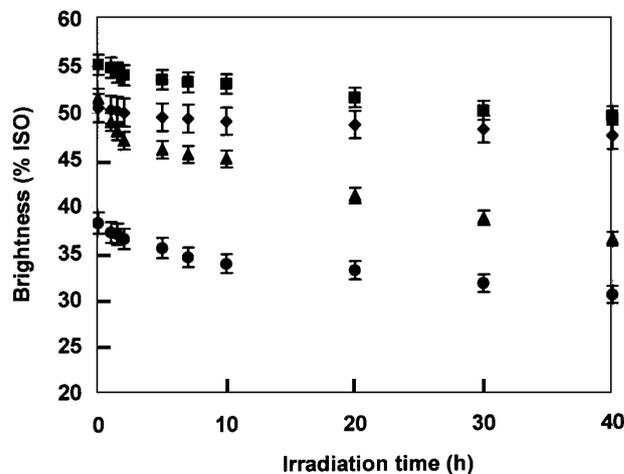


**Figure 4.** Relationship between the post colour (PC) number and acetylation time (min) of unbleached CMP paper samples. The relationship is given at two different irradiation times; 20 (■) and 100 (▲) h.

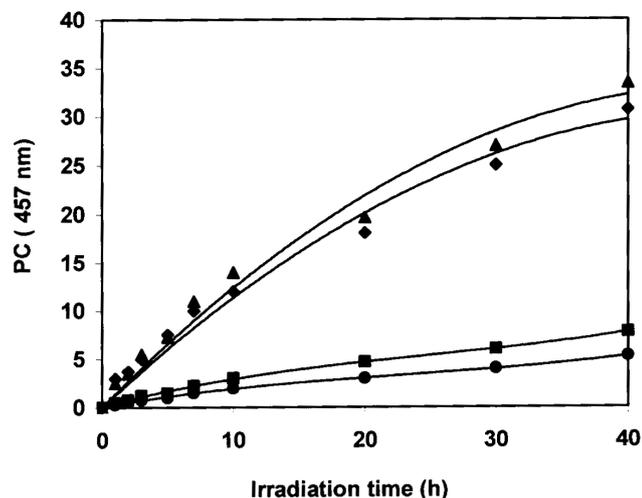
**Irradiation of Acetylated Unbleached Bagasse CMP**

The influence of acetylation on the degree of brightness reversion is indicated by PC number at 457 nm is shown in Figures 2 and 3.

As it evident in Figures 2 and 3, there is no considerable discrepancy between optical properties of paper samples because of the difference in temperature (80 or 100°C). Regarding to optical properties, the results obtained for 100°C shows slightly more resistance towards photo-discolouration comparing to 80°C. The acetylation treatment efficiently inhibited light-induced yellowing even after severe irradiation. It is clear that most of the photostabilization obtained appears after a

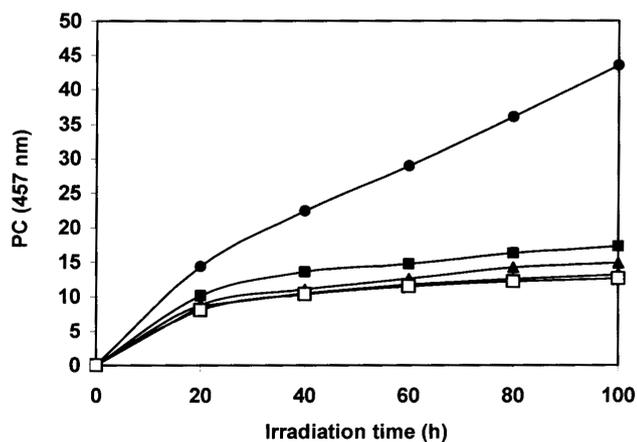


**Figure 5.** Effect of irradiation on brightness ( $R_{\infty, 457}$ ) for differently treated unbleached bagasse CMP papers. Control, (●); acetylated, (◆); NaBH<sub>4</sub>-reduced, (▲); NaBH<sub>4</sub>-reduced and acetylated, (■).

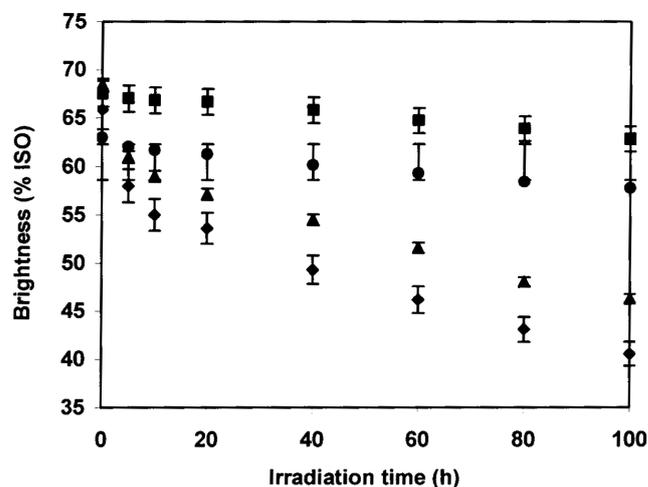


**Figure 6.** Effect of irradiation on post colour (PC) number of differently treated unbleached Bagasse CMP papers. Control, (◆); acetylated, (●); NaBH<sub>4</sub>-reduced, (▲); NaBH<sub>4</sub>-reduced and acetylated, (■).

short period of acetylation (Figure 4). Brightness changes due to irradiation have been illustrated in Figure 5. The yellowing rate of sodium borohydride and acetylated CMP paper sheets, declared as PC number, after photo-aging has been showed in Figure 6. As it could be seen in Figures 5 and 6, reduction with sodium borohydride, does not affect the process of yellowing of paper sheets. The brightness level of untreated papers was 33% after 40 h irradiation, i.e. a decrease of

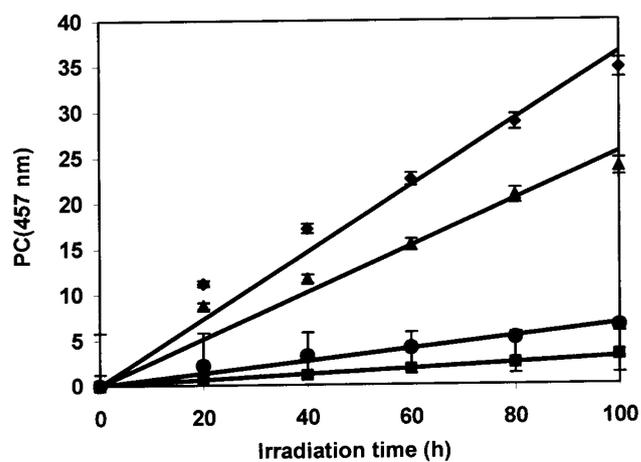


**Figure 7.** The effect of acetylation on the post colour (PC) number after accelerated long-term irradiation of hydrogen-peroxide-bleached and acetylated (100°C) hydrogen-peroxide-bleached bagasse CMP paper samples. The numbers in brackets denote the acetylation time (minutes). (●), control; (■), (10); (▲), (25); (◆), (60); (□), (120).



**Figure 8.** Effect of irradiation on brightness ( $R_{\infty, 457}$ ) for differently treated hydrogen-peroxide-bleached bagasse CMP papers. Control, (◆); acetylated, (●); NaBH<sub>4</sub>-reduced, (▲); NaBH<sub>4</sub>-reduced and acetylated, (■).

only 5 brightness units compared to the non-irradiated control. The corresponding value for the reduced papers was 41% (a decrease of more than 10 units). Acetylation efficiently preserves brightness value of the paper even after very intense irradiation. The PC number is less than 5 even after 20 h irradiation. The corresponding point for non-acetylated sodium borohydride reduced paper has been attained after 1-2 h irradiation. The effect of acetylation could be well evaluated by comparing the brightness changes followed by optical treatments [Figure 5]. The brightness of acety-



**Figure 9.** Effect of irradiation on post colour (PC) number of differently treated hydrogen-peroxide-bleached bagasse CMP papers. Control, (◆); acetylated, (●); NaBH<sub>4</sub>-reduced, (▲); NaBH<sub>4</sub>-reduced and acetylated, (■).

lated papers after 40 h irradiation was 50 % which still is 18% more than that unacetylated papers.

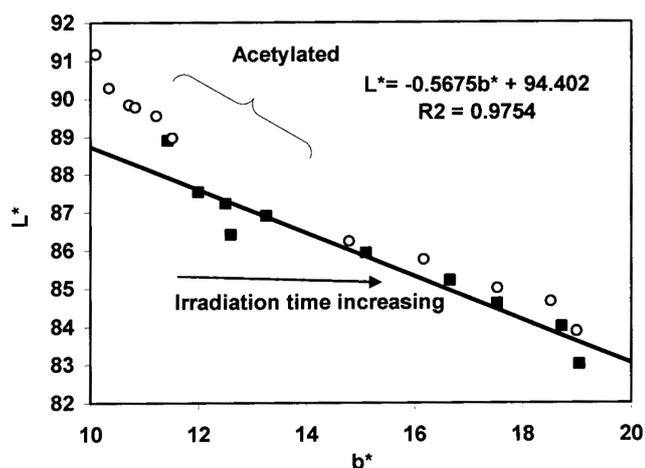
### Yellowing of Hydrogen Peroxide Bleached Bagasse CMP Papers

The influence of acetylation on the light-induced yellowing of hydrogen-peroxide bleached CMP paper samples is shown in Figure 7. As in the case of unbleached CMP; acetylation significantly retards the detrimental effect of light exposure. The structures causing discolouration of hydrogen-peroxide bleached CMP are easily derivatized on acetylation. However, the brightness levels after long-term irradiation of acetylated bleached paper samples were almost the same as the values obtained for acetylated unbleached CMP compared at the same degree of acetylation time. The increase in brightness of about 15 units that occurs on bleaching with  $H_2O_2$  could not be preserved by acetylation. As it could be seen the degree of yellowing of acetylated peroxide bleached CMP paper sheets is more pronounced than the yellowing of an acetylated unbleached CMP papers. The removal of most of the coniferaldehyde and quinonoid units in the lignin moiety during treatment with alkaline  $H_2O_2$  could be one explanation of the lower inhibiting effect observed with acetylated bleached CMP.

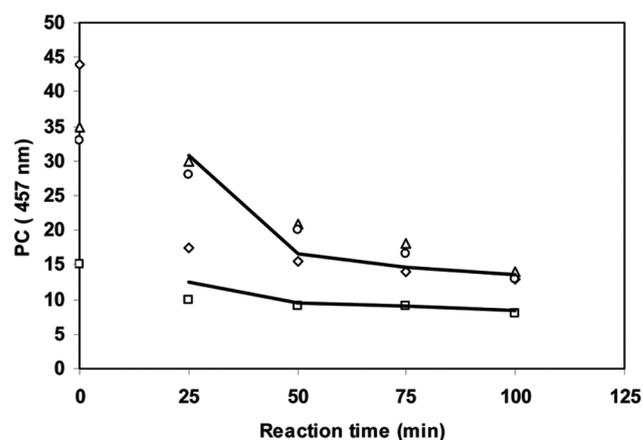
The influence of acetylation and reduction on the photo-yellowing of hydrogen peroxide bleached papers is shown in Figures 8 and 9. The brightness of peroxide bleached control papers reverted somewhat more than

the corresponding unbleached papers throughout the whole investigated irradiation interval. It was further found that the reductive treatment lowered the yellowing rate of the peroxide bleached papers compared with that of the untreated control. Acetylation increased the stability towards light-induced oxidation of both bleached CMP and reduced and bleached CMP papers in a manner analogous to that observed for unbleached papers. Brightness after 20 h irradiation was 57% for reduced, 61.3% for acetylated and 66.7% for reduced and acetylated bleached CMP papers. The corresponding value for the bleached control was 53.6%.

Figure 10 shows the lightness plotted against the yellowness for the differently treated bleached papers. Borohydride reduction eliminated chromophores responsible for the yellow colour, whereas acetylation generated structures that increased  $b^*$ . The lightness was in both cases unaffected by reduction and/or acetylation. Irradiation increased  $b^*$  and decreased  $L^*$  for all papers, but, the extent of the change was smaller for the acetylated papers. The results obtained from the reductive treatment indicate that the bleached CMP contained some photoreactive structures that could be partly eliminated or inactivated during reduction, whereas the colour-forming structures in unbleached CMP were unreactive towards  $NaBH_4$ -reduction (Figures 6 and 9). A similar result, for the first phase of yellowing (PC values up to 4), was reported for sodium borohydride stone groundwood pulp from spruce [34]. According to these authors, the limited effect of reduction on bright-



**Figure 10.** Lightness ( $L^*$ ) versus yellowness ( $b^*$ ) for hydrogen peroxide bleached bagasse CMP papers subjected to irradiation.



**Figure 11.** The effect of acetylation on the PC-number after accelerated light-induced aging (10 h) for differently treated bagasse CMP papers. The acetylation was performed at 100°C. ( $\square$ ), unbleached; ( $\diamond$ ), unbleached,  $NaBH_4$ -reduced; ( $\circ$ ), bleached; ( $\triangle$ ), bleached,  $NaBH_4$ -reduced.

ness stabilization indicates that cleavage of phenacyl aryl ether linkages is of minor importance in the initial phase of discolouration. Furthermore, reduction of peroxide bleached CTMP was reported to have no significant effect on chromophore formation [8]. It is, however, not possible conclusively to determine how carbonyl groups contribute to yellowing by a reduction experiment alone since the modest stabilization effect may be due to the incomplete reduction of carbonyl groups. The remaining ring-conjugated carbonyl groups could function as photo-sensitizers since trace amounts are enough to cause discolouration upon irradiation. It was suggested by Fournier de Violet et al. (1989) [8] that direct photolysis of phenolic hydroxyl groups might be essential in the photodiscolouration process. Furthermore, recent investigations have shown that irradiation of sodium borohydride reduced, hydrogen peroxide bleached TMP generated new aromatic ketone groups [13, 35]. Sodium borohydride is able to reduce quinones and carbonyl groups to hydroquinones/catechols and alcohol groups, i.e. structures that may be acetylated. In spite of this, reduction before acetylation did not affect the yellowing rate to any great extent. This is contradictory to earlier reported results for unbleached and bleached ground-wood pulps where sodium borohydride reduction before gas phase acetylation greatly diminished the stabilizing effect of acetylation [17].

There have been many suggestions to which functional groups in lignin are essential in the yellowing process. The phenolic hydroxyl group is an obvious candidate and many mechanisms involving a direct or indirect participation of this group have been suggested. The contribution of the phenolic group has not however yet been clarified

[18]. Alkylation of pre-reduced Norway spruce TMP with diazomethane or propylene oxide gave a resistance to light-induced yellowing comparable to that of fully bleached kraft pulp [12]. The acetylation experiments indicate that the brightness reversion can be significantly reduced or eliminated even at low degrees of acetylation. Figure 11 shows the relationship between PC-number and acetylation time. The inhibiting effect of acetylation seems to proceed more or less in two phases, an initial phase with a rapid decrease in chromophores formation followed by a slower phase. This means that there are some structures that can easily be removed by acetylation and which significantly

contribute to brightness reversion. The other leucochromophoric structures demand longer reaction times to be inactivated. It is also evident that acetylation is an efficient mean of stabilizing unbleached, bleached or reduced pulp and that the time, course and extent of stabilization are similar for all treated pulps. This suggests that the same structures are essential for the overall reaction and that these structures are still present in the pulp both after reduction and after hydrogen peroxide bleaching but are removed or inactivates during acetylation. These findings support the hypothesis that the phenolic hydroxyl groups play an important role in the yellowing reaction.

## CONCLUSION

The results obtained in this study demonstrate that the acetylation of paper manufactured from peroxide bleached Bagasse CMP significantly retards light-induced discolouration. The inhibition of yellowing is connected with a decrease in the phenolic hydroxyl content of both unbleached and peroxide bleached papers. This strongly supports the hypothesis that phenolic hydroxyl groups are involved in the discolouring reactions.

The reductive treatment did not affect the yellowing rate to any great extent; a small stabilization effect was observed for unbleached CMP were slightly more prone to discolour after long irradiation times. Borohydride reduction followed by acetylation had the same effect as acetylation alone when the comparison was made at the same degree of acetylation time.

## ACKNOWLEDGEMENTS

Financial support of Pyame Noor University and technical assistances of Pars pulp and paper Industries (Khuzistan, Iran) is fully appreciated. Also, we would like to thank Ms. Alizadeh and Mr. Safizadeh for their esteemed assistances during the experiments.

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