STUDYING THE EFFECT OF PHOTO-YELLOWING ON THE BRIGHTNESS PROPERTY OF CHEMI-MECHANICAL PULPING PAPER

MOHAMMAD NEMATI, AMIR HOOMAN HEMMASI,
MOHAMMAD TALAEIPOUR and AHMAD SAMARIHA

*Department of Wood and Paper Engineering, Science and Research Branch,
Islamic Azad University, Tehran, Iran*

Received November 11, 2011

The main objective of this study was to evaluate and determine the variation in brightness characteristics of chemi-mechanical papers, which were produced by Mazandaran Wood and Paper Company through treatment with some transitional metal ions in addition to relevant techniques to decrease it. The existing metal ions in chemi-mechanical pulps lose their brightness upon reaction of the paper fiber with lignin. Although some of their properties will be increased, including yellowness, the brightness of the pulps produced through mechanical or chemi-mechanical procedures are preferred according to investigations on the aging degree and other relevant brightness parameters. Some unbleached samples of paper were prepared at the factory and then, they were treated using following two chemical materials. Firstly, they were wetted using EDTA (Ethylene Diamine Tetraacetic Acid) as chelating agent, at various levels of concentration. The process neutralized available ions in the samples of CMP (chemi-mechanical papers) and also the existing metal ions, which can trigger aging and yellowness regimes. Secondly, after EDTA-wetted samples were dried, they were wetted again by solutions containing transitional element ions.
The obtained results revealed that the most prevalent effect on brightness improvement was associated with Fe^{2+} ions, while the least considerable one was related to ions of Al^{3+}. Similar to a neutral ion, Al^{3+} did not show a significant effect on decreasing the brightness. Besides, when the samples were wetted using different concentrations of EDTA, a significant decrease occurred in detrimental effects, reducing the brightness and increasing the yellowness degrees.

Keywords: accelerated optical aging, brightness, EDTA, hardwood CMP, transitional metal ions

INTRODUCTION

Several methods have been considered to decrease the negative effect of ions, one of them being the use of chelating agents.[1] Since chelating materials employed in previous experiments, such as DTPA, are rather expensive, emphasis here will be put on inexpensive substitutes, like EDTA. Improvement in durability without causing negative effects on brightness, physical properties, and strength of CMPs is one of the main targets for all manufacturers. Since the chemi-mechanical process produces part of the paper consumed in Iran, it is important to study optical properties, as well as solutions to mitigate yellowness and aging effects. Ions of transitional metals, such as Fe^{2+}, Cu^{2+}, and Mn^{2+}, cause paper to be colored.[2] The affinity of these ions to react with lignin and form colorful complexes in samples produced from species containing high lignin contents is greater than in those with lower lignin contents. During a typical pulping process, water, equipments, and even wood chips can act as sources of transitional metal ions. Using distilled water is not economically feasible to mitigate the negative effects of ions. Thus, some alternative methods have been suggested, namely using chelating elements like EDTA, decreasing pH value of the pulp,[1] and acetylation.[3] Scientifically speaking, paper produced from chemi-mechanical pulp is composed of cellulose, hemicelluloses, lignin, extractive materials, additives, starch and starching materials, fillers, and pigments. Mechanically produced and high-yield pulps, such as CMP with a lot of lignin, will intrinsically experience decline in whiteness and brightness, or the well-known "yellowness" phenomenon in the absence of light, or in the presence of light and UV waves in the 300-400 nm range with higher amplitudes. Researchers have shown that light-induced coloring will be intensified by oxygen, while humidity does not affect it much.[4] Carter focused on colors of pulps that contain great amounts of lignin. He argued that under light, heat, humidity, presence of active ions (Ca^{2+} and Fe^{3+}), and gas pollutants (especially SO_2 and NO_2), yellowing will occur due to oxidation and photo-oxidation of chemical groups in paper, in addition to the creation of new colorful groups.[2] Ek *et al.* assessed the light-induced yellowing mechanism of acetylated pulps from ground wood (GW). The effect of partial acetylation on light-induced yellowness of unbleached pulps, pulps bleached with hydrogen peroxide, and GW pulps reduced with borohydride showed that the quinone compounds in light-induced oxidized pulps prior to acetylation have catalyzed chemical reactions.[5] Saint *et al.* evaluated the addition of yellowness inhibitors in mechanical pulps. They quantified the kinetic stability and equilibrium of 2-benzotriazole (as inhibitor of yellowness) by studying variations in type and density of the inhibitor and also concentration of the salt under study.[4] Qiu *et al.* focused on DTPA in order to decompose peroxide using the Mn ion. The effect of metal ions, such as Mn^{2+}, on the decomposition behavior of hydrogen peroxide was assessed using DTPA as an inhibitor. The results indicated that the addition of DTPA to Mn^{2+} containing pulp was more effective that the pulp without DTPA addition.[6]

Mirshokraei has studied the effect of metallic ions on optical properties of CMP, which was prepared from hardwood species. DTPA was utilized as the chelating material in his experiment. In this regard, pulp supplied from Mazandaran Wood and Paper Company was pre-treated with DTPA first. Then, it was bleached by hydrogen peroxide under specific conditions. After reducing the pH values and bleaching, distilled water, metallic ion containing water, tap water, and industrially used water were selected to implement light-induced accelerated aging procedures on the handsheet paper samples. Based on observations and results from this test, the most detrimental effect on optical properties, yellowness and aging phenomena were attributed to the Fe^{2+} ion, while the least detrimental effect was related to ions of Al^{3+}. Furthermore, the presence of the DTPA chelating agent caused brightness stability to be increased.[1] Veysi studied the coloring of steeled CMP pulps prepared from two species of beech through light-induced and heat-induced aging. The obtained results were indicative of the fact that upon acetylation, steel groups simply replaced hydrogen in the lignin phenolic hydroxyl, thereby blocked the motion of the electrons in phenyl propane units. The stability of brightness increased because light-absorbing quinones were not formed.[7]

Evaluating the effects of transition metal ions on optical properties and studying the effect of photo-yellowing on brightness property of chemi-mechanical pulping paper are the main objectives of this research, and, specifically, which ions have the highest effect on the optical properties.

EXPERIMENTAL

Unbleached CMP pulp samples were supplied by Mazandaran Wood and Paper Company. For better saturation and absorption, samples of smaller dimensions were prepared. Since some samples were wrinkled so that they could cause difficulties in measuring the optical properties, a saturation method was used instead of a spray. Generally speaking, two series of samples were used: (1) control sample (without any treatment), (2) sample treated with EDTA and metallic ion containing solutions. For the second series, the ions present in CMP paper samples were neutralized after saturation with EDTA chelating agents. Once dried, the samples were exposed to saturation with each of the solutions incorporating metallic ions. Research reports often refer to employing DTPA as chelating agent. The concentration of this material in the production line of Mazandaran Wood and Paper Company is of approximately 0.3%. EDTA chelating agent has been applied with various concentrations in experiments, however the optimal concentration of EDTA in decreasing the detrimental effect of ions was of 0.5%. In this study, EDTA chelating agent has been employed to investigate its application to substitute DTPA, given its lower price. The effect of EDTA was evaluated for 0, 0.25, 0.5, 0.75 and 1% concentration levels. In order to produce EDTA-containing solution, deionized water was used instead of tap water to prevent errors in test results and avoid the negative effect of ions available in tap water. The pH value of the EDTA solution was set in the range of 5.5 to 6.

Using salts of metallic ions soluble in water, such as nitrates and sulfates, had a significant importance in making solutions containing metallic ions of transitional elements. Deionized water was preferred to drinking water and industrial water in preparing metallic ion containing solutions. The question "How effective is each one of the metallic ions?" is answered by their concentration in the water consumed at factory. The following salts were used to produce solutions containing metallic ions:

$FeSO_4.7H_2O$ – $CuSO_4.5H_2O$ – $MnSO_4.H_2O$ – $FeCl_3.6H_2O$ – $AlCl_3.5H_2O$

The concentrations of these ions were determined based on their common contents in the water consumed by the factory as below:

Fe^{3+}	Fe^{2+}	Cu^{2+}	Al^{3+}	Mn^{2+}
1 ppm	0.3 ppm	0.1 ppm	25 ppm	1 ppm

Drying the samples was done in an environment without light and moisture, since paper samples were prone to absorbing optical waves and to yellowing as they were saturated with EDTA and metallic ions. Mild fan blowing was used to dry the samples under the afore-mentioned conditions. A simulated apparatus was also used for accelerated light-induced aging experiments. Six UV lamps of Black Light made by Philips were used in addition to four regular fluorescent lamps. The output frequency had a typical range of 300 to 400 nm. Light-induced treatments were implemented in time spans of 0, 10, 20, 30, 40 and 50 hours. Technibrite Micro TB-1C spectrometer apparatus was utilized to measure the brightness of papers. All measurements were carried out on the basis of Tappi-T452-OM-98 standard.

Data analysis was directed by SPSS software, while multi-domain Duncan test was used for separating the average values and studying the individual and mutual effects of each variable.

RESULTS AND DISCUSSION

Table 1 summarizes the data obtained for brightness characteristics versus variables of time, EDTA concentration and metallic ions in the bleached CMP samples. The increase in time duration will always decrease the brightness content and thus the aging number. The same trend is repeated for all ions and EDTA concentrations. Higher concentrations of EDTA will cause the brightness index to be decreased at lower ratios. In fact, it is the chelating agent that raises the brightness stability and improves the brightness properties.

Table 1
Brightness characteristics of CMP paper samples at different times and concentrations of EDTA and metal ions

Ion concentration	EDTA%	0 h	10 h	20 h	30 h	40 h	50 h
	0	52.11	44.90	42.41	41.80	40.27	39.35
	0.25	52.23	45.01	42.76	42.21	40.43	39.86
0.3 ppm Fe^{2+}	0.5	52.13	46.26	43.39	42.11	41.05	40.20
	0.75	52.37	46.83	44.28	41.21	41.87	39.92
	1	52.15	47.31	44.89	41.12	41.06	40.13
	0	52.29	46.73	44.39	42.76	41.39	40.11
	0.25	52.11	47.23	45.24	43.81	41.15	41.02
1 ppm Fe^{3+}	0.5	51.89	47.66	45.36	34.82	42.01	41.83
	0.75	52.23	48.07	46.11	44.39	42.25	41.11
	1	52.22	48.31	43.76	43.76	42.11	40.89
	0	52.27	46.83	43.59	43.83	41.09	40.31
	0.25	52.23	46.89	44.63	43.73	40.83	40.52
0.1 ppm Cu^{2+}	0.5	52.11	47.91	45.61	43.87	41.66	41.02
	0.75	51.89	47.36	46.80	43.21	41.14	41.05
	1	52.21	47.30	45.06	44.21	41.36	40.83
	0	52.20	47.09	44.63	43.90	40.89	40.58
	0.25	52.41	47.27	44.83	43.86	41.29	40.39
1 ppm Mn^{2+}	0.5	51.83	47.83	45.01	43.73	40.72	41.06
	0.75	52.06	48.21	45.83	43.70	41.25	41.09
	1	51.93	47.83	46.11	43.80	48.36	40.75
	0	51.89	51.19	50.29	49.39	40.39	47.72
	0.25	52.42	51.39	50.47	49.11	49.81	47.83
25 ppm Al^{3+}	0.5	52.30	51.02	51.21	50.12	49.73	48.25
	0.75	52.11	51.11	50.80	50.02	49.63	48.43
	1	52.13	51.61	51.03	50.73	49.63	48.81

Table 1 reveals that the most effective ion on decreasing the brightness is Fe^{2+}, while Al^{3+} acts as the least effective one. Table 2 summarizes the multi-directional variance analysis on the brightness characteristics of the unbleached CMP samples versus time, concentration of EDTA and metallic ions, as different variables. All variable parameters had a meaningful impact on the brightness content with each of them being able to change that value significantly.

The study on the mutual effect of each variable in Table 2 revealed that the effect of each variable on other variables was also significant. The evaluation of the ion-EDTA mutual effect shows that the increase in concentration of this chelating agent, regardless of the effect of metallic ions on improving brightness properties, has been able to significantly enhance and stabilize the brightness properties as well.

Although there have been some negative effects from metallic ions on the brightness characteristics (Fe^{2+} being the most and Al^{3+} the least effective ions), EDTA has enhanced the stability of brightness. Meanwhile, considering the impact of each ion on brightness variations, EDTA has caused brightness to be decreased with much less intensity. Besides, studying the mutual effect of the two variables of ions and time demonstrates that the time has always been able to decrease the brightness significantly. In other words, time lapse for the Fe^{2+} ion, with the most prevalent impact on brightness, has decreased the brightness and increased the yellowness characteristics.

Table 2
Multidirectional variance analysis for brightness characteristics of CMP samples versus variables of time, EDTA and metallic ion concentration

Source of variation	Sum square	Degree of freedom	Mean square	Statistical F	P value
Ion	718.214	4	179.554	1229.639	0.000
EDTA	10.208	4	2.552	17.477	0.000
Time	1717.088	5	343.418	2351.832	0.000
Ion-EDTA	4.731	16	0.296	2.025	0.021
Ion-time	185.332	20	9.267	63.461	0.000
Time-EDTA	5.239	20	0.262	1.794	0.035
Error	11.682	80	0.146		
Total	2652.492	149			

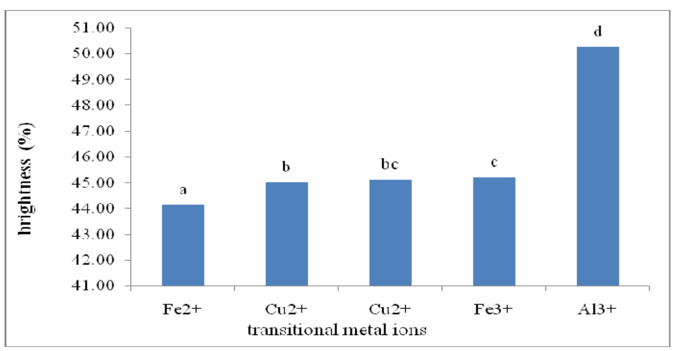


Figure 1: Duncan test results for studying the effect of ion variable on brightness characteristics of unbleached samples (lowercase letters indicate Duncan ranking of averages at 5% confidence interval)

Time lapse has also reduced brightness for the neutral ion of Al^{3+}. Emphasis on the mutual effect of the two variables of time and EDTA uncovered that though time lapse has yielded higher brightness, the increase in the EDTA caused brightness to be decreased in light-induced aging times at lower ratios. This means that the increased EDTA has noticeably improved brightness properties for all aging times.

Since all three elements have been identified as effective in accordance to Table 2, the question whether all levels of different variables are effective in decreasing the brightness may be put forward. Based on Fig. 1, it can be argued that from the variables of metallic ions with an effect on the brightness of the unbleached CMP samples in Duncan test, as to increased yellowness, decreased brightness, brightness stability and quality of brightness, the most significant is associated with Fe^{2+} ion, while the least significant with Al^{3+}. These results are in good agreement with those offered in Table 1. In other words, the average values for yellowness characteristics are significant for all metallic ions. Ni *et al.* concluded that Fe^{2+} can be simply oxidized into Fe^{3+}, their bleaching potential being increased.[8] Then, Fe^{3+} ion will have the ability to change yellowness and brightness characteristics significantly.[9]

Figure 1 depicts the effect of time and EDTA concentration on decreasing brightness characteristics of the unbleached samples saturated by Fe^{3+} ions. It is clear that the curves associated with a lower concentration of EDTA are placed higher. The level of the curves descends as the EDTA concentration decreases and it provides smaller brightness changes, which are increased with much lower ratios.

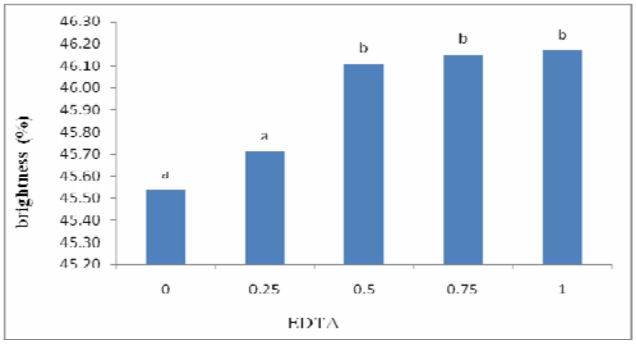


Figure 2: Duncan test results for studying the effect of EDTA variable on brightness characteristics of unbleached samples (lowercase letters indicate Duncan ranking of averages at 5% confidence interval)

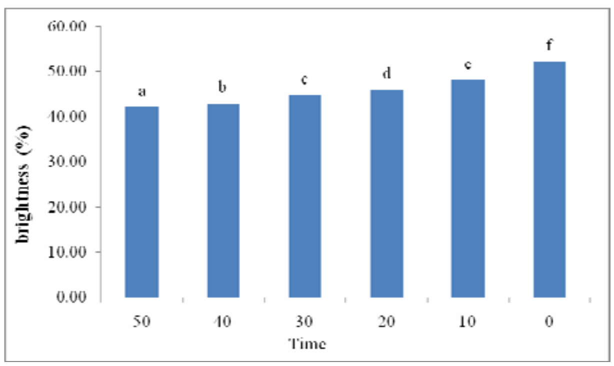


Figure 3: Duncan test results for studying the effect of time variable on brightness characteristics of unbleached samples (lowercase letters indicate Duncan ranking of averages at 5% confidence interval)

The investigation on different contents of the EDTA chelating agent, called Duncan test, has been illustrated in Fig. 2. The main objective here was to study the effect of the EDTA variable parameter on the brightness properties of the unbleached CMP, as well as its effect in promoting the brightness properties. It is obvious that the concentrations greater than 1% are able to impose significant changes on the brightness index. Although the optimal range of applying chelating agents is of 0.5% and its usage can determine some improvements in the brightness properties, this solution is not economically feasible.

Figure 3 shows the results obtained for Duncan test in studying the effect of time variable on brightness characteristics of the unbleached CMP samples. It demonstrates that the increase in time from 0 to 50 hours will cause significant changes on the brightness content.

Generally speaking, the brightness of the unbleached CMP samples have Fe^{2+} and Al^{3+} as the most and the least effective ions, respectively. This finding is in accordance with the results reported by other researchers.[1,10]

$Al^{3+} < Mn^{2+} < Cu^{2+} < Fe^{3+} < Fe^{2+}$

The mechanism of chromophore formation and lignin destruction due to yellowing, as well as lignin photo-oxidation, is discussed below.

Primary chromophores from lignin: absorption of light with 300 to 400 nm wavelengths → break of etheric bonds and creation of free radicals → reaction between free radicals and lignin → formation of ketyl radicals →phenoxy and ketone radicals → production of yellow quinone and chromophores with secondary chromophores→ light-induced destruction of lignin and yellowing of paper.[7]

Several arbitrary factors participate in high-yield pulps, such as oxygen, structure of α-carbonyl, binary bonds of lignin, free oxygen, free radicals, several types of peroxides, phenollic groups (i.e. cathecole), orthoquinones, paraquinones (i.e. methoxi-p-benzoquinone), β-O-4 lignin, hydro quinones, and acetylene created from phenylcoumaran.[11]

Researches show that acetylene exists in high-yield and unbleached pulps with peroxies.[1,7] Furthermore, active oxygen-containing compounds, such as hydroxyl radical (HO°), hydroperoxyl radical (HOO°), alchoxy radical (RO°), alkyl proxy radical (RO_2°), anionic radical (O^{-2}°), oxygen groups ($3O_2$), oxygen (O_2), oxygen atoms of O° (from ozone), and hydrogen peroxide (H_2O_2) are some examples of chemical compounds, which are partial reasons for the oxidation process. Cellulose and lignin chromophores are known as the yellowing agents in paper.[12]

Cellulose is a homopolysaccharide in which anhydrous cellobiose units are repeated (1.03 nm). Tshriner *et al.* stated that carbonyl and carboxyl groups were formed from anhydrous glucose units upon oxidation or photo-oxidation[13]. Saint *et al.* designated oxidized hemicelluloses chromophores as aldehyde groups on C_2 and C_3 carbon atoms. Lignin is an aromatic polymer that is composed of phenyl propane units with etheric bonds present its structure at a lower content of C-C bonds.[4] Ek *et al.* declared that the contributions of oxidized cellulose and hemicelluloses produce the minimum yellowness in lignin-containing papers, since the contribution of coloring lignin groups are more significant than cellulose and hemicelluloses.[5] Haque *et al.* argued that aromatic ketones, quinones, aldehydes and acids would be due to the photo-oxidation behavior of lignin.[11] The general structure of lignin and metallic complexes is schematically shown in Scheme 1, where M_2 is the metallic ion.

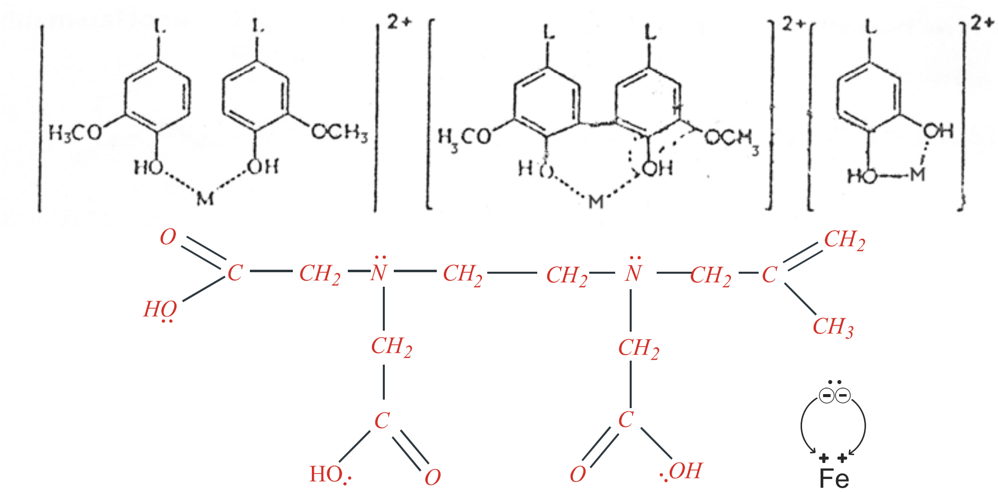
Thus, all pairs of oxygen-electron will chelate metallic ions and surround them. So they will not let them form stable complexes with lignin, which may incur optical damages to lignin and cause yellowness of paper.

In order to improve brightness parameters and prevent unfavorable characteristics, such as yellowness, some techniques have been proposed, namely methylation[11] and removing yellowness-making elements (quinones).[7]

Observing the statistical results obtained for yellowness and brightness characteristics of bleached and unbleached samples implies that the parameter of time has also played a key role in modifying the yellowness characteristics. Thus, the results are indicative of a significant effect of time on the brightness characteristics. In other words, increasing the time duration has improved these characteristics significantly. On the other hand, brightness properties have also been subjected to other parameters, such as ion type, concentration of the chelating agent, time of light-induced aging, and lignin content of the samples. Fe^{2+} has additionally provided the greatest impacts on brightness characteristics, either as a completely effective or as a destructive ion. It has incurred more detrimental impacts in comparison with other ions due to formation of oxygen-bearing radicals, which can be attributed to the accelerated creation of phenoxy radicals by Fe^{2+} ions. Chelating agents, including EDTA, have a positive effect and cause the brightness characteristics to be decreased in lower ratios as time elapses. Meanwhile, brightness content will experience a little decrease versus accelerated light-induced aging time, which can be attributed to the more reactive EDTA, in addition to the formation of stable constants with the metallic ions. In other words, the chelating material, such as DTPA and EDTA, will confine the ion and will avoid its destructive function.

However, using chelating materials has some limitations from the scientific and economic points of view, it is not economical to use these materials in higher concentrations. It is not possible to expect higher effects for increased concentration values, because the optimal limitation of application for this material is of about 0.5% and its maximum limit of application is almost 1%. Above this level, no effect on yellowness improvement can be observed, and neither is it economically feasible to utilize this material in high contents.

The general mechanism associated with the chelating materials, including DTPA, EDTA and DTPAMP, is that the metallic ions form very stable complexes with phenolic composition[3] having high stability constant. However, chelating agents such as EDTA will create more stable complexes with metallic ions due to their more reactive conditions.



Scheme 1: General structure of lignin and metallic complexes

Therefore, ion-EDTA complexes will reach better thermodynamic equilibriums when paper samples are saturated with EDTA, by increasing the concentration of EDTA, the effect of metallic ions will become less pronounced.

Generally speaking, the contribution of coloring lignin is more significant for the unbleached samples that contain more lignin and extractive materials, since the role of oxidized cellulose and hemicelluloses is minimized in decreasing brightness of the paper.[10]

The pulping process with optical brightness agents (OBA) does not have effective roles or significant effects on the whiteness of the unbleached pulps and papers, but it will reduce the yellowness (b*).[13]

CONCLUSION

The following techniques have been put forward as effective ways to enhance the optical properties of papers, increase their brightness stability, stop or mitigate yellowing, stop light-induced coloring or aging of CMPs: modifying the primary chromophores, reduction by sodium borohydride,[3] using chelating agents,[1] employing inhibitor agents (which prevent yellowness of the mechanical pulps i.e. amine hydroxyl),[13] reduction in pH value of the pulp (due to lower durability of the metallic ions),[6] acetylation,[3] and methylation.[10]

REFERENCES

[1] S. A. Mirshokraei, *Iran. J. Nat. Res.*, **58**(**2**), 405 (2005).

[2] H. A. Carter, *J. Chem. Educ.*, **73**(**11**), 1068 (1996).

[3] V. N. Gupta, D. B. Mutton, *Pulp Pap. - Canada*, **70**(**6**), 77 (1969).

[4] K. Saint-Cyr, T. G. M. de Ven and G. Garnier, *J. Pulp Pap. Sci.*, **28**(**3**), 78 (2002).

[5] M Ek, H. Lennholm, G. Lindblad and T. Iversen, *Nordic Pulp Pap. Res. J.*, **7**(**3**), 108 (1992).

[6] Z. Qiu, Y. Ni and S. Yang, *J. Wood Chem. Technol.*, **23**(**1**), 1 (2003).

[7] R. Veysi, Ph.D. Thesis, Islamic Azad University, Sciences and Research Branch, 2005, p. 166.

[8] Y. Ni, A. Ghosh, Z. Li, C. Heinter and P. McGarry, *J. Pulp Pap. Sci.*, **24**(**8**), 259 (1998).

[9] M. Paulsson, A. J. Ragauskas, *Nordic Pulp Pap. Res. J.*, **13**(**2**), 132 (1998).

[10] B. H. Yoon, L. J. Wang and G. S Kim, *J. Pulp Pap. Sci.*, **25**(**8**), 289 (1999).

[11] M. N. Haque, H. P. S. Abdul Khalil and C. A. S. Hill, *Journal of Timber Development Association of India*, **54**(**3**), 25 (2002).

[12] A. J. Latibari, *Polym. Sci. Technol. Mag.*, **17**(**4**), 247 (2004).

[13] U. Tshriner and C. W. Dence, *Pap. Puu*, **36**(**4**), 338 (1998).