

USE OF NITROGEN CENTERED PEROXIDE ACTIVATORS TO INCREASE THE BRIGHTENING POTENTIAL OF PEROXIDE

II. OPTIMIZED CONDITIONS

Q. Y. HU,* C. DANEAULT,** and S. ROBERT*

**Centre de Recherche sur les Matériaux Lignocellulosiques, Université du Québec à Trois-Rivières, Trois-Rivières (Québec), Canada G9A 5H7*

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This work focuses on a new TAED/H₂O₂ bleaching system on spruce-balsam thermomechanical pulp, at low consistency. The experiments show that the TAED/H₂O₂ system improves the brightness of the softwood thermo-mechanical pulp significantly (6% ISO), compared to the peroxide system alone. For each fixed molar ratio of TAED/H₂O₂, there is an optimum range for alkali addition, for achieving a maximum brightness gain of the thermomechanical pulp, a well-defined linear correlation being found between the TAED/H₂O₂ molar ratio and the optimal alkali charge. An optimal TAED/H₂O₂ ratio is obtained at 0.7, slightly higher than the theoretical value of 0.5, as due to the saponification reaction of TAED. TAED/H₂O₂ results in pulps being slightly more susceptible to light-induced yellowing in the UV and visible regions of the spectrum, at very long irradiation times. Short term light-induced yellowing is approximately the same for both kinds of pulps.

Keywords: tetraacetylenediamine, TAED, hydrogen peroxide, activators, peroxyacetic acid, bleaching, yellowing

INTRODUCTION

Hydrogen peroxide has always been a technologically attractive oxidant for the pulp and paper industry. Extensive investigations have been carried out on the H₂O₂ bleaching of mechanical pulps.¹⁻³ High brightness mechanical pulps are difficult to produce only by applying successive peroxide stages.

Establishing methods for such activation or catalysis peroxide has been the subject of many researches devoted to chemical pulp bleaching. Peroxide activated with polypyridines, as well as peracids, have been examined as potential systems for reinforcing oxygen delignification.⁴

The use of polyoxometalates (POM systems) has also been reported to activate the peroxide bleaching stages of eucalyptus kraft pulp under acidic conditions.⁵ Cui and co-workers⁶ investigated the reactivity of lignin towards hydrogen peroxide catalyzed by a binuclear manganese complex, and

suggested that hydrogen peroxide catalyzed by Mn(IV)-Me₄DTNE would be capable of oxidizing the α -hydroxyl groups and the conjugated C-C double bonds in the residual lignin of chemical pulps.

The literature contains numerous accounts and experiments made with various peroxide activators. The cyanamide activated peroxide bleaching process of chemical pulps was proposed by Sturm.⁷ Alkaline hydrogen peroxide was thought to react with cyanamide, to form a peroxyimidic acid intermediate. This species should have a higher oxidation than peroxide.

Edwards⁸ has pointed out that, generally, the peroxyacetic acid is considered better than the hydrogen peroxide, which is capable of reacting with the electron pair-donors (R₂S, Br⁻, etc.) 10⁵ more rapidly than the hydrogen peroxide. Hauthal *et al.*⁹ have reported that peroxyacetic acid is a more active bleaching agent than hydrogen

peroxide, because the redox potential of peroxyacetic acid is higher than that of hydrogen peroxide.

Shao¹⁰ has shown that the use of a TAED/H₂O₂ bleaching system can be efficiently used, as well, for bleaching cotton fabrics within shorter times than the regular bleaching processes, because of the *in situ* generation of peracids and of the safety issues involved in the direct manipulation of peracids.

Davies *et al.*¹¹ have shown that hydrogen peroxide and water react with tetraacetylenediamine (TAED), subsequently forming triacetylenediamine and diacetylenediamine, which is accompanied by the release of 2 molecules of peracetic or acetic acid. As a peroxide activator, TAED is a compound with N-bounded acetyl groups, nitrogen centered, able to react with the nucleophilic hydroperoxy anion, to yield peroxyacetic acid¹² or peracetic acid.¹³

Cround and Mathews¹⁴ have examined the effect of adding tetraacetylenediamine (TAED) in alkaline peroxide delignification. Depending on the pH of the bleaching stage, TAED is thought to react with peroxide to produce peracetic acid or a peracetate anion. Both species are known to be stronger oxidants than hydrogen peroxide. Under alkaline conditions (pH 9-10), TAED rapidly reacts with the peroxide. Coucharrière and co-workers,^{15,16} who studied the factors affecting the kinetics of peroxide kraft pulp delignification with TAED, confirmed that, in alkaline peroxide stages, TAED is beneficial only at reduced temperatures, therefore proving a better delignifying action of the peracetate anions, compared to that of perhydroxyl anions. However, compared to a standard peracetic acid (PAA) treatment, better delignification was obtained with the TAED/H₂O₂ system.

Leduc *et al.*¹⁷⁻¹⁹ have evaluated the efficiency of adding oxidizing agents, such as hydrogen peroxide, peroxide/TAED, either in a post-bleaching operation or in the refiner process of mechanical pulp. The use of an activator (TAED) in a conventional medium consistency bleaching allows significant improvements in the brightness level of the thermomechanical pulp and a reduction in the temperature applied.

While our previous study²⁰ about the kinetic of a lignin model compound,

acetovanillone (4'-hydroxy-3'-methoxyacetophenone) in TAED/H₂O₂ and peroxide-alone systems focused on the reaction mechanism and kinetics, the main objective of the present investigation is to evaluate the potential of the TAED activator on alkaline peroxide bleaching of thermomechanical pulp at low consistency. The effects of the TAED charge, alkali charge, TAED/H₂O₂ molar ratio and initial pH were examined.

MATERIALS AND METHOD

The bleaching results were obtained with a commercial thermomechanical pulp of spruce/balsam from an Eastern Canadian newsprint mill. The initial brightness of pulp, after DTPA pre-treatment, is of 58.2% ISO. Upon receipt, the pulp was diluted to 3% consistency with deionized water at 60 °C, and stirred for 30 min with 0.5% DTPA on o.d. pulp. The suspension was thickened in a centrifuge to 20% consistency and then stored in sample bags in a refrigerator at 4 °C. Transition metal analysis of the pulp after treatment with DTPA yielded 34 ppm Fe, 12 ppm Mn, and 2 ppm Cu. The nitrogen centered peroxide activator was tetraacetylenediamine (TAED).

Bleaching procedures

Bleaching studies were carried out in a glass reactor maintained at 60 °C in a water bath of constant temperature. The pulp suspension was continuously mixed. The experimental conditions for bleaching with hydrogen peroxide and activated peroxide are: pulp consistency – 1%, at 60 °C for 60 min with 0.05% MgSO₄ and 3.00% Na₂SiO₃, for a total alkali ratio modulated between 0.3 and 1.7. The TAED/H₂O₂ molar ratio applied varied between 0 and 1.1. After bleaching, pH is measured, and the pulps are neutralized to destroy the bleaching agents, while the pH is adjusted to 5.5, to minimize brightness reversion. The method applied for the neutralization of pulps consists in diluting the pulp to 4% consistency with a neutralizing agent (sodium metabisulfite, Na₂S₂O₅), mixing the slurry for 5 min, followed by pulp pressing after 15 min. After neutralization, two samples are used to make standard brightness pads, obtained with deionized water, on a British sheet machine, following the Tappi method T218 om-91. The brightness and color coordinates were measured on a Technibrite, according to the Tappi standard method T452 om-92.

Peracetic acid and hydrogen peroxide concentrations were measured by iodometric titration.

Brightness stability

Paper handsheets (10 g/m²)²¹ made from bleached pulps were used to determine the

kinetics of photo-oxidation, with a UV-visible spectrophotometer (Cary 3, Varian) equipped with a diffuse reflectance integrating sphere. Photo-oxidation was performed at room temperature, in a merry-go-round photochemical reactor (Rayonet) equipped with 16 RPR-3500Å lamps, for a total of 24 W, between 300 and 420 nm, emitting a photon flux of 1.5 to 5×10^{16} photons/s/cm³. The irradiation of papers was done in cumulative exposures of up to 60 h, which roughly corresponds to a full year of continuous irradiation to sunlight.

RESULTS AND DISCUSSION

TAED/H₂O₂ in alkaline medium

In the first part of the study, the effect of the molar ratio (TAED/H₂O₂) on brightness was investigated for 1% pulp slurry. Bleaching experiments were conducted at constant temperature (60 °C), with hydrogen peroxide at 3.5% and total alkali at 1.5%, for 60 min. The results are presented in Figure 1.

Coucharrière *et al.*¹⁶ reported that, when peroxide and TAED were applied in an alkaline medium at pH 11 and 60 °C, the decomposition of PAA would take approximately 13 min.

To achieve a maximum brightness gain of the thermomechanical pulp, there is an optimum range for TAED addition. The maximum brightness level with TAED (63.7%) is slightly higher when compared with peroxide alone (63%). A TAED/H₂O₂ molar ratio of 0.2 gives the maximum brightness, while any higher ratio will lower the brightness response. These results were similar to those reported by Leduc.¹⁷⁻¹⁹ In these works, a TAED/H₂O₂ molar ratio of 0.3 gives the maximum brightness. Better bleaching results have been obtained with lower quantities of bleaching activator, although, theoretically, the highest quantity of peracetic will be produced at a TAED/H₂O₂ molar ratio of 0.5. The initial pH observed in Figure 1 can be also explained by the competitive decomposition reaction of peracetic acid, as shown by Zhao *et al.*¹³ Thus, apart from the molar ratio, pH and alkali charge adjustments are required to optimize the bleaching conditions when the TAED charge increases.

TAED charge

Figure 2 shows the effect of various amounts of TAED with various alkali charges introduced prior to the alkali

peroxide-TAED bleaching process. It is shown that, for each fixed TAED/H₂O₂ molar ratio, there is an optimum range for alkali addition, to achieve a maximum brightness gain of the thermomechanical pulp. The optimal alkali charge level depends on the TAED/H₂O₂ molar ratio.

Alkali charge

The effect of various charges of alkali introduced prior to the alkali peroxide-TAED bleaching process is presented in Figure 3. There is an optimum range for the addition of alkali for achieving a maximum brightness gain of the thermomechanical pulp with a fixed TAED/H₂O₂ molar ratio of 0.2.

An alkalinity level of peroxide bleaching liquor of 3% gives the maximum brightness; any higher alkali charge will lower the brightness response. The maximum brightness level with TAED (65.5%) is higher than that of the peroxide alone (64%). For two systems, TAED-peroxide and peroxide alone, the alkali charge with the maximum brightness level is different. Apparently, an optimal point of the alkali charge should be considered, as a function of the different TAED/H₂O₂ molar ratios, to achieve the maximum brightness.

Thus, the TAED effect should not be compared without adjusting the alkali charge, as illustrated in Figure 2. It is important to point out that, for studying the effect of various amounts of TAED introduced prior to alkali peroxide bleaching, the maximum brightness point should be first found out for each fixed TAED/H₂O₂ molar ratio, at various alkali charges.

Maximum brightness at optimum alkali charge

Figure 4 shows the relationship between the maximum brightness obtained at each fixed TAED/H₂O₂ molar ratio vs. the TAED amount. It is obvious that, when using the TAED activator, the brightness of the thermomechanical pulp is higher, compared to that of the peroxide alone, more TAED resulting in a higher brightness level.

A TAED/H₂O₂ molar ratio of 0.7 gives the maximum brightness, after which, even if the amount of TAED increases, brightness will remain constant.

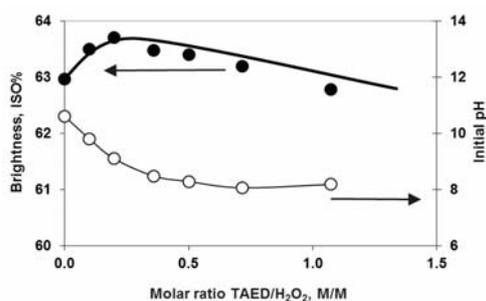


Figure 1: Effect of molar ratio TAED/H₂O₂. Bleaching temperature – 60 °C, 3.5% H₂O₂, 1.5% total alkali, reaction time – 60 min

A maximum of 6% ISO brightness points with TAED have been gained, compared to peroxide alone.

This curve basically confirms the theoretical tendency. However, there are still some slight differences between our investigation and the theory. In our study, the optimal TAED/H₂O₂ molar ratio for maximum brightness is of 0.7, vs. the theoretical value of 0.5. According to Hauthal,⁹ just about 1.5 mole of peroxyacetic acid is formed from 1 mole of TAED bleaching activator. Theoretically, the formation of 2 moles of peroxyacetic acid from 1 mole of bleaching activator should be expected, without neglecting the saponification reactions of DADHT or TAED with the hydroxide anion, which could explain why the maximum brightness can be attained at a TAED/H₂O₂ molar ratio of 0.7 and not of 0.5 (the theoretical molar ratio). There is no need to continue to

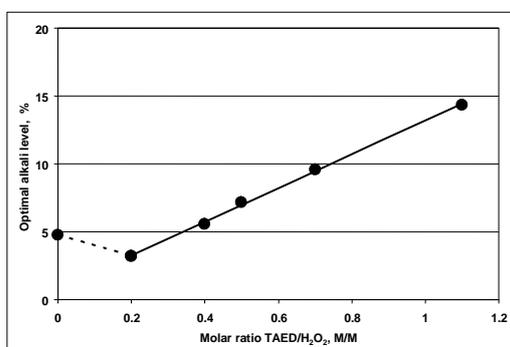


Figure 3: Optimal alkali as a function of TAED/H₂O₂ molar ratio

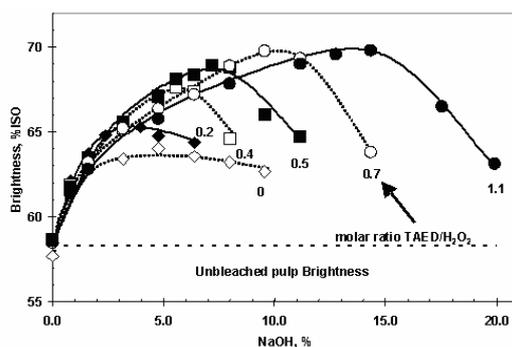


Figure 2: Brightness as a function of alkali charge at various TAED/H₂O₂ molar ratios (0.2, 0.4, 0.5, 0.7, 1.1). Conditions: 1% pulp, 6% H₂O₂, t – 60 min, T – 60 °C

increase the TAED/H₂O₂ molar ratio, because a plateau has been attained in the concentration of peroxyacetic acid formed and, since the peroxyacetic acid is the main oxidizing bleaching chemical present, brightness gain will be constant above a 0.7 molar ratio.

pH

The main role of the alkali is to maintain the required pH of the bleaching liquor, for obtaining peroxyacetic acid and for promoting the bleaching reaction of the pulp. Figure 5 shows the initial pH of the TAED/H₂O₂ bleaching liquor, which gives a maximum brightness at a fixed TAED/H₂O₂ molar ratio and optimal alkali charge, being obvious that the optimal initial pH level is around 11, increasing slightly with increasing the TAED/H₂O₂ molar ratio.

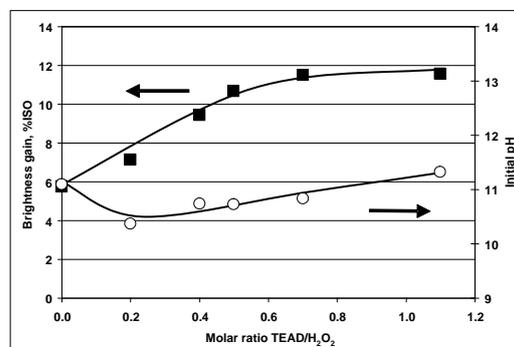


Figure 4: ISO brightness and pH variation for optimal conditions as a function of TAED/H₂O₂ molar ratio

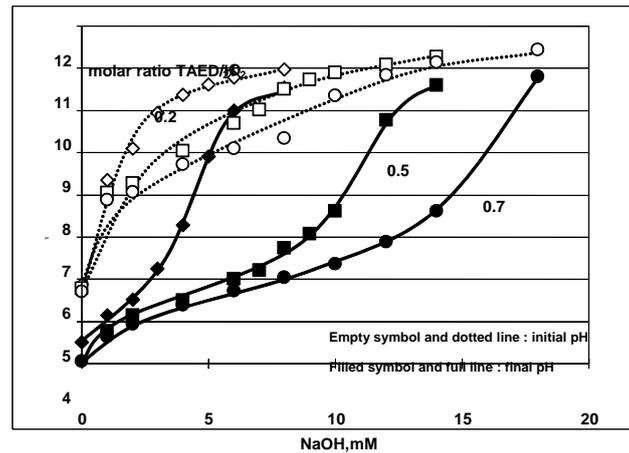


Figure 5: Measured pH with TAED/H₂O₂ system during bleaching process. TAED/H₂O₂ ratios are of 0.2 (diamonds), 0.5 (squares) and 0.7 (circles)

Table 1
pH measured in TAED/H₂O₂ system under optimal conditions

Molar ratio TAED/H ₂ O ₂ , M/M	Alkali charge, %	Brightness, % ISO	Initial pH	Final pH
0.2	3.2	65.4	10.37	7.28
0.4	5.6	67.7	10.74	7.30
0.5	7.2	68.9	10.73	7.08
0.7	9.6	69.7	10.83	6.88
1.1	14.3	69.0	11.32	6.68

Table 2
Yellowing kinetics constants

At 420 nm: $k_t = k_\infty + A_1 e^{-c_1 t} + A_2 e^{-c_2 t}$								
	k_∞ (m ² .kg ⁻¹)	A_1 (m ² .kg ⁻¹)	$c_1 \times 10^{-4}$ (min ⁻¹)	A_2 (m ² .kg ⁻¹)	$c_2 \times 10^{-4}$ (min ⁻¹)	$ A_1 + A_2 $ (m ² .kg ⁻¹)		
H ₂ O ₂	35.98	-25.54	9.305	-6.595	153.9	32.14		
TAED/H ₂ O ₂	39.06	-27.69	7.081	-6.835	156.3	34.53		
At 350 nm: $k_t = k_\infty + A_1 e^{-c_1 t} + A_2 e^{-c_2 t} + A_3 e^{-c_3 t}$								
	k_∞ (m ² .kg ⁻¹)	A_1 (m ² .kg ⁻¹)	$c_1 \times 10^{-4}$ (min ⁻¹)	A_2 (m ² .kg ⁻¹)	$c_2 \times 10^{-4}$ (min ⁻¹)	A_3 (m ² .kg ⁻¹)	$c_3 \times 10^{-4}$ (min ⁻¹)	$ A_1 + A_2 + A_3 $ (m ² .kg ⁻¹)
H ₂ O ₂	32.35	-38.15	2.783	16.50	341.5	-12.397	2.007	34.05
TAED/H ₂ O ₂	59.78	-12.62	2.138	5.511	4 411	-52.702	18.10	59.81

However, according to Figure 5, to get the maximum brightness, by the end of the prescribed reaction time, the pH should be around 7. This means getting the maximum brightness at a fixed TAED/H₂O₂ molar ratio, while the initial pH of the TAED/H₂O₂ bleaching liquor should be adjusted to a high level, *i.e.* about 11, and the final pH should be kept at a neutral level, *i.e.* about 7. Table 1 shows the optimal pH level attained for each TAED/H₂O₂ molar ratio, at an optimal alkali charge.

Brightness stability

Color reversion study shows an increase of the light absorption coefficient, LAC, in time, as expected from numerous literature reports. Figure 6 shows the LAC behavior after various irradiation times, of up to 60 h, for a TAED/H₂O₂ bleached pulp. The H₂O₂ bleached pulp exhibits a very similar behavior. In both cases, two spectral regions are of particular interest: the 350 nm and 420 nm regions, associated with conjugated coniferaldehyde or carbonyl groups and

ortho-quinone structures. In both cases, LAC variation can be examined as a function of time: the results are presented in Figure 7.

One can see that the yellowing kinetics at 420 nm, for both TAED/H₂O₂ and H₂O₂ bleached pulps (white and grey circles), is almost identical. The kinetics can be easily fitted, at 420 nm, to a double exponential reaction of the type:²²

$$k_t = k_\infty + A_1 e^{-c_1 t} + A_2 e^{-c_2 t}$$

where c_1 and c_2 are the rate constants of chromophore formation, and A_1 and A_2 are related to the quantity of chromophores created.²³ These values are shown in Table 2.

This equation clearly indicates that there are at least two reaction pathways leading to the formation of *o*-quinones (at 420 nm), as already shown in literature.^{24,25} The behavior observed in the coniferaldehyde region (around 350 nm, white and grey squares) is quite different. Upon UV light irradiation, the chromophores absorbing light at 350 nm are destroyed in a first phase, after which two reaction mechanisms create more structures that absorb light in this region. Such a behavior was previously observed in literature with thicker handsheets,²⁶ and can thus be fitted to a triple exponential like:

$$k_t = k_\infty + A_1 e^{-c_1 t} + A_2 e^{-c_2 t} + A_3 e^{-c_3 t}$$

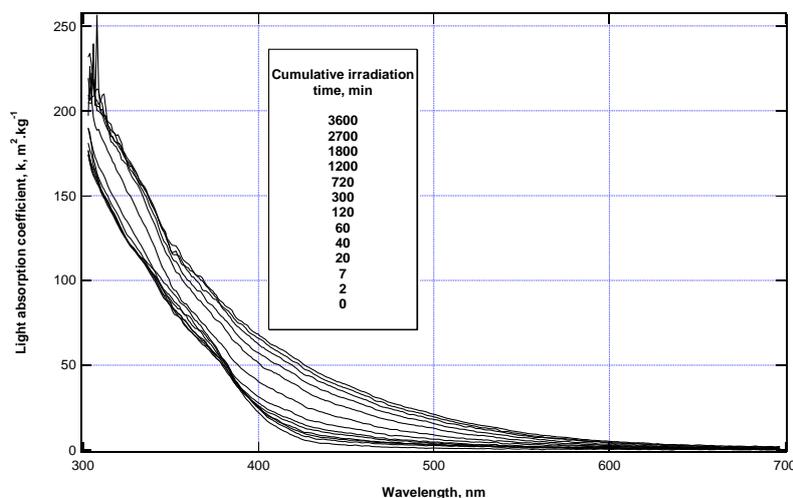


Figure 6: Light absorption coefficient variation as a function of wavelength after various irradiation periods of up to 60 h for a TAED/H₂O₂ bleached pulp

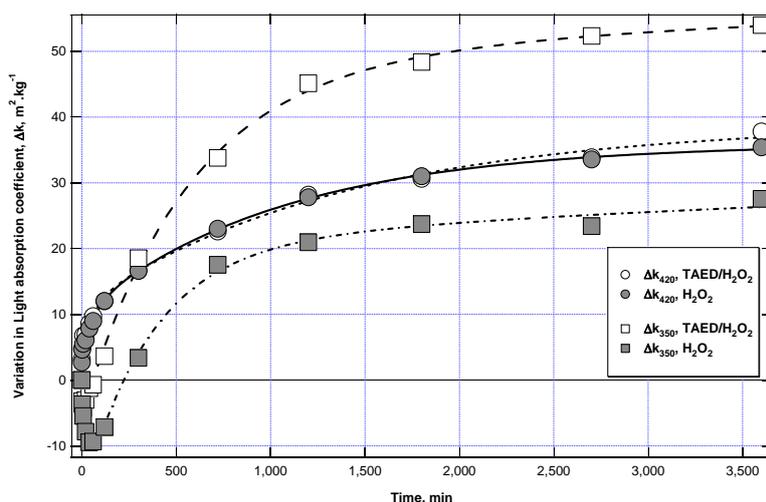


Figure 7: Light absorption coefficient variation as a function of time at two selected wavelengths, 350 and 420 nm, for both TAED/H₂O₂ bleached and H₂O₂ bleached pulps

From k_∞ , as well as from the $|A_1 + A_2|$ value at 420 nm, both the H₂O₂ and the TAED/H₂O₂ bleached pulps show similar results upon light-induced yellowing, but with a slightly higher final LAC value for the

TAED/H₂O₂ bleached pulp. This indicates that the TAED/H₂O₂ pulp is slightly more susceptible, by about 8%, to UV-light-induced yellowing than the H₂O₂ bleached pulp.

Again, the behavior at 350 nm is quite different for both pulps, resulting in about 80% more coniferaldehyde-type chromophores created in the TAED/H₂O₂ bleached pulp, comparatively with the H₂O₂ bleached pulp. This is more evident if we look at the LAC values after 60 h, as shown in Figure 8, with the difference spectrum showing the increase in coniferaldehyde-type chromophores.

Proofs are thus pointing to a difference in the yellowing reaction mechanism for pulps bleached in the presence of TAED. The difference is not big at 420 nm, but it is quite substantial at 365 nm, which indicates that pulps bleached in the presence of TAED are,

as a general rule, slightly more susceptible to light-induced yellowing in the visible region of the spectrum at very long irradiation times, and more susceptible in the UV region. The short term light-induced yellowing is almost the same for both kinds of pulps. This can be probably explained by the results of Hsieh *et al.*,²⁷ who showed that hydrogen peroxide generates more methoxyhydroquinones than the peracetic acid, which can lead to the modification of the post-color number, as methoxyhydroquinones are known to undergo secondary reactions leading to the formation of chromophores.

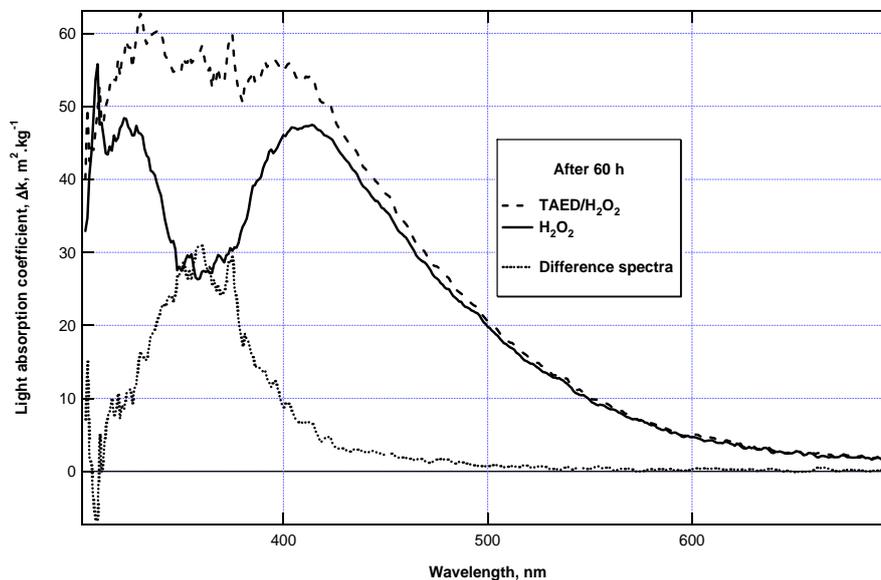


Figure 8: Light absorption coefficient values after 60 h of UV irradiation for both TAED/H₂O₂ bleached and H₂O₂ bleached pulps, and the difference spectrum

CONCLUSIONS

Under the conditions applied in the study, the experiments performed show that the TAED peroxide system improves significantly the brightness of softwood thermomechanical pulp, approximately 6% ISO more brightness being achieved by this TAED/H₂O₂ system comparatively with the peroxide-alone system. For each fixed molar ratio of TAED/H₂O₂, there is an optimum range for alkali addition, to achieve the maximum brightness gain of the thermomechanical pulp. This means that, for attaining the maximum brightness, an adjustment of the alkali charge is indispensable, along with the increase of the TAED charge, a well-defined linear correlation being found between the molar

ratio of TAED/H₂O₂ and the optimal alkali charge. By this linear correlation, one can easily find an optimal alkali charge for a fixed TAED/H₂O₂ molar ratio, to attain the best brightness level under the conditions of this study. The maximum brightness gain increases gradually when the TAED/H₂O₂ molar ratio is between 0 and 0.7 while, when the ratio is higher than 0.7, brightness will not increase, any more, regardless of the ratio. This optimal ratio point of 0.7 is a little higher than the theoretical value of 0.5, as a result of the saponification reaction of TAED. According to pH data, it is very clear that the optimal initial pH level should be about 11, while the end pH level is of about 7, under both these pH level conditions, the TAED/H₂O₂ system giving an optimum

brightness level for the thermomechanical pulp. TAED/H₂O₂ results in pulps being slightly more susceptible to light-induced yellowing in the visible region of the spectrum, at very long irradiation times. Short term light-induced yellowing is almost the same for both kinds of pulps.

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