Metal management improves peroxide bleaching of TMP

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ABSTRACT

Several pretreatments of a commercial thermomechanical pulp were carried out to maximize peroxide bleaching by sequestering metal ions with a series of sequestering agents such as DTPA; EDTA; HEDTA; DTPMPA; and dibenzo-18, crown-6 ether. Iron, copper, magnesium, and manganese concentrations were monitored by atomic absorption spectroscopy. A concentration of 0.5% of these agents is sufficient to sequester the maximum amount of metal ions. Consistency, temperature, and retention time have no effect on the chelation efficiency of manganese.

On the other hand, pH is an important factor in chelation. HEDTA is an excellent sequestrant in an acidic pH condition. However, DTPMPA demonstrated better chelation of manganese in alkaline conditions. An HEDTA pretreatment in an acidic pH condition increases ISO brightness of TMP by 6.8 points compared to 4.5 points for conventional bleaching, where DTPA is used in both chelation and bleaching stages. For a nonpretreated thermomechanical pulp, DTPMPA is the best agent to be used in the bleaching liquor, decreasing peroxide consumption from 1.9 to 1.45%. To optimize the optical properties and peroxide consumption, different combinations of sequestering agents in pretreatment and bleaching stages were investigated. The most effective metal chelation is adding DTPMPA in the bleaching liquor to bleach an HEDTA-pretreated TMP. This sequence yields maximum brightness and minimum peroxide consumption. A clear two-point gain in brightness can be achieved over a DTPA control system.

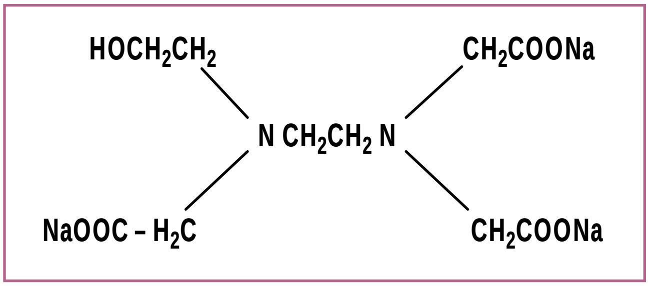
The pulp and paper industry has greatly evolved through the past decade. Environmental considerations forced the mills to make certain changes in pulp production and bleaching technologies. In the 1960s, bleached and crude chemical pulps were the most widely used, considering their high quality and brightness. However, their low yield and their bleaching processes are very polluting because of the use of chlorine. For this reason, high-yield pulps have risen in popularity; therefore, their bleaching technologies must be optimized to decrease costs. Hydrogen peroxide is the most effective bleaching agent used today, achieving the greatest brightness gain. However, this agent is expensive, and its bleaching capacity needs to be maximized. It is important that secondary undesirable reactions with peroxide be minimized. The most destructive secondary reaction known is the catalytic decomposition of peroxide by metal ions. Equation 1 reveals the global reaction leading to this phenomenon *(1)*.

$$H_2O_2 + M^{2+} \rightarrow M^{3+} + OH^- + OH^-$$
$$H_2O_2 + M^{3+} \rightarrow M^{2+} + M^+ + OOH^-$$
$$OOH^- \rightarrow O_2 + H^-$$
$$H^- + OH^- \rightarrow H_2O$$
$$H^+ + OH^- \rightarrow H_2O$$

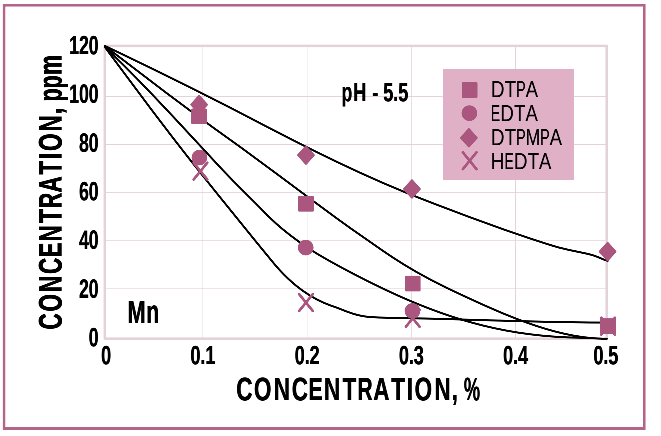
The most important metal ions responsible for catalytic decomposition, in decreasing order of catalytic capacity, are Mn > Fe > Cu *(2)*. Literature suggests that the catalytic effect increases in alkaline media *(3)*. Metal ions, such as aluminum and calcium, have a lesser effect on peroxide decomposition. However, high concentrations of these ions may provoke color reversion *(4)*. Ions such as Mn^{2+} and Cu^{2+} catalyze auto- oxidative reactions and accelerate brightness reversion, leading to the formation of colored structures in lignin. The Fe^{3+} ion forms highly colored complexes with lignin *(5)*. A 2.5-point brightness drop occurs when 120 ppm of Fe^{3+} is added to the pulp *(6)*.

Diethylene-triaminepentaacetate (DTPA) is the most common sequestering agent used in the industry due to its great stability in oxidative bleaching *(8)*. The electrons from the five oxygen atoms and the free electron doublet from the three nitrogen atoms form the eight legends of this chelating agent. These legends participate in the formation of the chelate with the metal ions. Ethylenediaminetetraacetate (ETDA) is another agent used commercially, but unlike DTPA, this molecule has six legends. Kuczynski has reported a maximum gain of about 5 ISO points due to the chelation of pulp before bleaching with 2% peroxide *(9, 10)*. Each sequestering agent chelates different quantities of metal ions. EDTA at a concentration of 0.5% decreases manganese 96%. DTPA at the same concentration decreases the manganese content 79% *(11)*. It is expected that the phosphoamines or oxygen-formed legends could help in pulp chelation. Hydroxyethylenediaminetetraacetic acid (HEDTA) [Fig. 1], diethylene triamine pentamethylene phosphonic acid (DTPMPA), and crown ethers are three classes of chelating agents that, depending on their chemical functions, are expected to demonstrate variable degrees of chelating efficiency toward metal ions.

The objective of this study is to optimize metal chelation of high-yield pulps to maximize hydrogen



1. HEDTA



2. Mn concentration after chelation vs. agent concentration

peroxide bleaching efficiency. The present work involves optimizing the chelating efficiency of metal ions using novel sequestering agents either in combination with conventional sesquestrants or separately. First, the effect of the pretreatment conditions on the chelating efficiency of given agents was studied. Bleaching trials then followed to evaluate the bleaching capacity of the pulp to justify the necessity to optimize metal profiles in a pretreatment stage. Finally, different combinations of sequestering agents in pretreatment and bleaching stages were examined to maximize the optical properties and minimize consumption of peroxide.

EXPERIMENTAL

A thermomechanical pulp (TMP) (spruce/balsam) from a Canadian mill was supplied for the trials throughout this study.

Sequestering conditions.

Using the commercial chelants DTPA and EDTA, parameters such as chelant concentration, consistency, reaction time, and temperatures were varied. DTPMPA and HEDTA were also used for conducting trials varying the pH level and concentration. Consistency was studied between 1 and 5%, reaction time between 5 and 30 min, temperature between ambient and 60°C, and pH between 4 and 10.

Different chelants, such as DTPA; EDTA; HEDTA; DTPMPA; and dibenzo-18, crown-6 ether, were examined for their sequestering ability. A concentration of the chelants fixed at 0.5% was applied to the pulp at 3% consistency and at a temperature of 60°C for 15 min. Two washing stages at 2% consistency followed the reaction period. The pulp was then pressed at 30% consistency. Pulp samples were ashed and the ashes digested with hydrochloric acid. Atomic absorption spectroscopy was performed to determine iron, copper, magnesium, and manganese concentrations.

Bleaching trials

Two percent hydrogen peroxide bleaching trials were carried out at pH 11 and at 12% consistency for 2 hours. Various chelants were added in the bleaching liquor to determine whether it is beneficial for brightness gain. Bleaching liquor was sampled at the end of the run to measure peroxide residual. Peroxide was neutralized and the pH was adjusted to 5.5 with sodium metabisulfite. The pulp was then washed twice at 1% consistency with deionized water. Bleaching pads were made, and optical properties such as brightness and CIE L*,a*,b* coordinates were measured according to TAPPI Test Methods.

RESULTS AND DISCUSSION—CHELATION

Effect of the sequestering conditions.

Conventional chelating agents are normally used at 0.5% concentration, at 60°C, with a minimum exposure time of 15 min at a pulp consistency of 3%. With the urge to maximize bleaching efficiency, it was thought that the pretreatment conditions could have an effect on the metal ion removal. Preliminary experiments indicated that most chelants have a maximum response on manganese. Therefore, we considered the monitoring of manganese for the experiments where the pretreatment conditions were optimized. The manganese content for the following trials was 120 ppm.

Chelant concentration

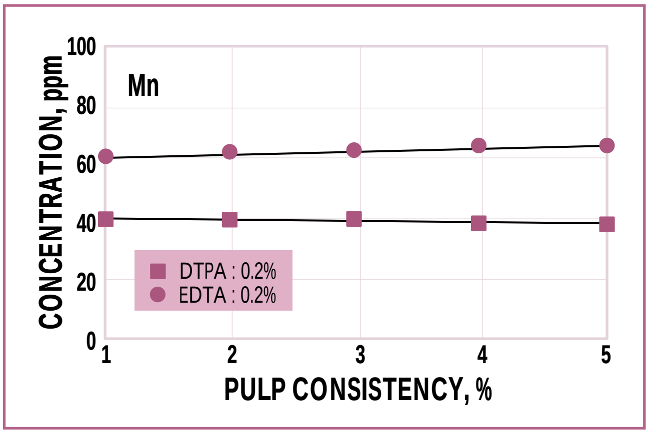
Figure 2 illustrates the manganese removal upon chelation for agent concentrations varying from 0 to 0.5%. HEDTA has the greatest chelating efficiency within the four sequestrants examined. Inversely, DTPMPA does not chelate manganese effectively at pH 5.5. The other chelants effectively remove this metal when applied at 0.5% concentration.

Pulp consistency

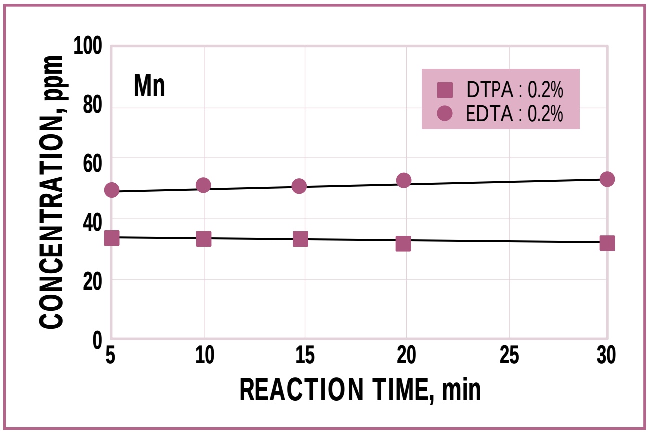
Figure 3 illustrates the manganese concentration after the sequestering stage for pulp consistency ranging from 1 to 5% using 0.2% of both DTPA and EDTA, respectively. These results show that there is no significant change in chelation efficiency for manganese for the range of consistency studied.

Temperature

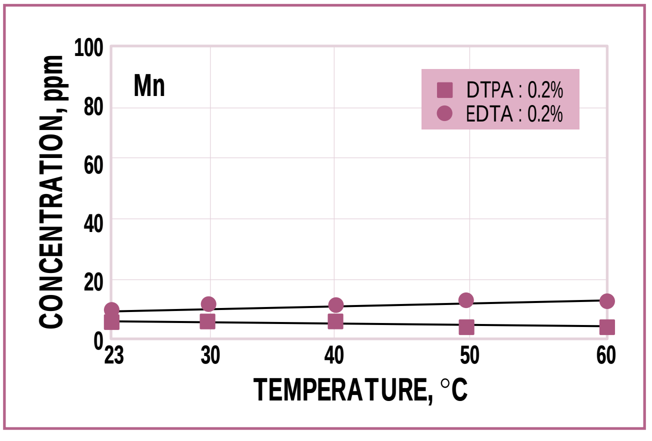
The residual concentration in manganese after chelation for temperatures ranging from 23 to 60°C using 0.5% of both DTPA and EDTA is



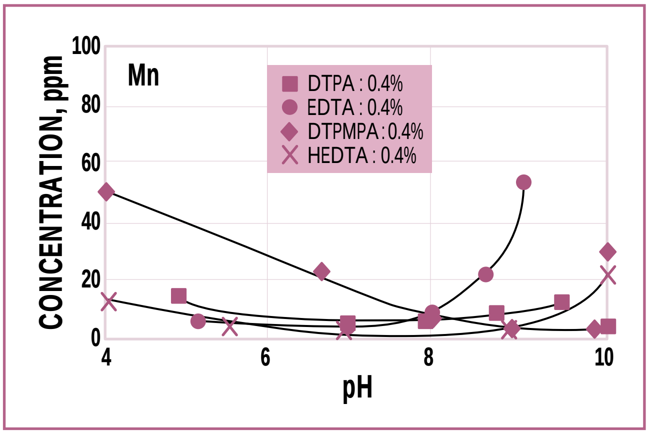
3. Mn concentration after chelation vs. consistency



5. Mn concentration after chelation vs. reaction time



4. Mn concentration after chelation vs. temperature



6. Mn concentration after chelation vs. pH

illustrated in Fig. 4. The results show no significant change in chelation efficiency for temperatures included in this range.

Reaction time

Residual manganese concentration after chelation for reaction times varying from 5 to 30 min using 0.2% of both DTPA and EDTA is illustrated in Fig. 5. As with pulp consistency and temperature, reaction time has no significant effect on the chelation efficiency of manganese for a reaction time less than 30 min.

Effect of pH

Figure 6 illustrates the relationship between the pH of sequestration and the residual manganese content in the pulp using 0.4% of DTPA, EDTA, DTPMPA, and HEDTA. The results show that varying the pH from 4 to 10 does not affect the chelating efficiency of DTPA and HEDTA on manganese. Unlike DTPA, the chelating efficiencies of manganese for EDTA and DTPMPA depend on the pH used. For EDTA, chelating efficiency is unchanged up to pH 8 and decreases beyond this pH level. DTPMPA's chelating efficiency is much greater at alkaline pH levels. Therefore, DTPMPA could be used in the alkaline peroxide bleaching condition to sequester metal ions, leading to the possible elimination of the pretreatment stage.

Chelant comparison

Metal profile

Iron, copper, magnesium, and manganese concentrations of the TMP pulp used in this part of the study were 128, 1.5, 255, and 82 ppm, respectively. Table I shows the conditions used in the chelation stage for the comparison of various chelating agents. All sequestering trials were conducted at pH 5.5.

Parameter	**Condition**
Consistency, %	3.00
Temperature, °C	60
Time, min	15
pH	5.5
Chelating agent, %	0.5
Washing stage, %	2.0
Pressing stage, %	30

I. Conditions used for comparison of chelants

The results following the effect of the chelant treatment on the metal content are summarized in Table II. Decreasing the copper content is less obvious since it is very low. Although it is difficult to quantify copper chelation within our experimental variation, we found that HEDTA has a marginal edge over EDTA, decreasing the copper content to 0.8 ppm. DTPMPA decreased the copper content to 1.0 ppm. The iron content is decreased to approximately 109 ppm with either DTPA, HEDTA, or DTPMPA. Furthermore, DTPMPA is the only agent that sequesters magnesium, decreasing its concentration to 115 ppm. Acidic conditions are not favorable for the sequestration of manganese by DTPMPA. Manganese is however successfully removed with the use of DTPA and HEDTA to 3 ppm. Dibenzo-18, crown-6 ether compares to EDTA for the sequestration of manganese.

It is then apparent that an effective sequestration of manganese and copper can be effected by pretreating pulp in acidic pH conditions and then adding DTPMPA in alkaline conditions in the bleaching liquor.

Treatment* pH = 5.5	Copper (Cu)	Iron (Fe)	Magnesium (Mg)	Manganese (Mn)
None	1.5	128	255	82
DTPA	1.3	110	250	2.8
EDTA	1.3	126	252	6.6
HEDTA	0.8	109	245	3.1
ETHER	1.4	127	229	63
DTPMPA	1.0	108	115	30

*0.5% chelant used, 3.0% consistency, 60°C, 15 min. Experimental error varied from 2% to 5%.

II. Effect of chelation on metal ion content

Agents	Concentration
Sequestering agent, %	0 or 0.50*
Sodium hydroxide, %	1.60
Magnesium sulfate, %	0.05
Sodium silicate, %	3.00
Hydrogen peroxide, %	2.00
Consistency, %	12
Temperature, °C	70
Time, h	2

*Used as received: DTPA, EDTA, HEDTA 40% active; DTPMPA 50% active.

III. Bleaching conditions used

RESULTS AND DISCUSSION—BLEACHING

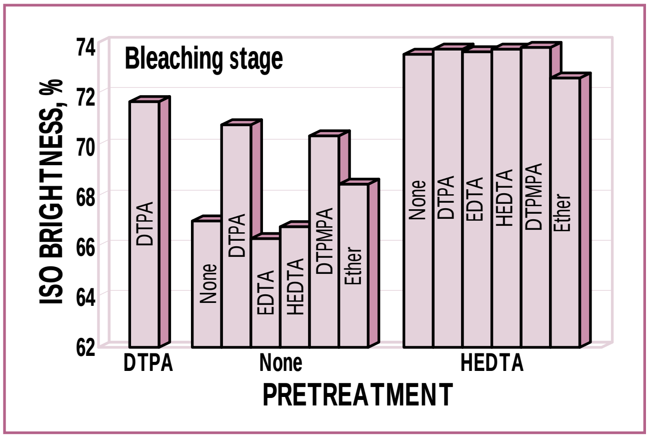
Hydrogen peroxide bleaching of chelated and nonchelated pulps was carried out according to the condition prescribed in Table III. Since the most common chelating agent used in peroxide bleaching is DTPA, results for DTPA used in the pretreatment and bleaching stages will serve as a basis for comparison. Results from Fig. 7 show the effect of chelation on the TMP bleaching for various sequestering agents. DTPMPA compares to DTPA in bleaching efficiency when used in the bleaching liquor on a nonchelated pulp. Adding either EDTA or HEDTA does not improve the brightening of a nonchelated thermomechanical pulp. Dibenzo-18, crown-6 ether aids brightness gain only by 1.5 points.

Although crown ethers contain sufficient oxygen legends for metal chelation, they are insoluble in the aqueous phase. For this reason, the diffusion and penetration of these chelants into the pulp are difficult; this results in poor sequestration.

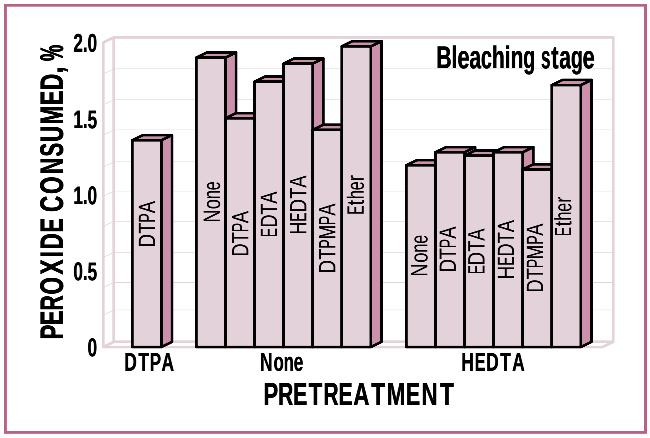
Bleaching efficiency is enhanced on pretreating the same pulp with HEDTA, increasing ISO brightness by 6.8 points compared to 4.5 points when using the most common DTPA sequence. The improved bleaching efficiency of HEDTA may be attributed to an optimum overall chelation of Cu, Fe, and Mn, which is not provided by either DTPA or EDTA. It is demonstrated that no significant brightness gain is obtained in adding a sequestering agent in the bleaching liquor when bleaching an HEDTA- chelated thermomechanical pulp. Only a minor improvement in brightness was achieved with the addition of DTPMPA.

Figure 8 illustrates the quantity of peroxide consumed after the bleaching stage for various sequences of pretreatment and bleaching stages. As in Fig. 7, results for DTPA used in the pretreatment and bleaching stages will equally serve as a basis for comparison. For a nonpretreated thermomechanical pulp, DTPMPA is the best agent to be added in the bleaching liquor, decreasing peroxide consumption from 1.9 to 1.45%. The addition of DTPA and EDTA in the bleaching liquor helps decrease peroxide consumption from 1.9 to 1.5 and 1.7%, respectively. There is no advantage in adding HEDTA or dibenzo-18, crown-6 ether in the bleaching liquor to reduce peroxide consumption upon brightening a nonchelated pulp.

A pretreatment of TMP with HEDTA in acid condition (pH = 5.5) not only improves brightness but also decreases peroxide consumption from 1.9 to 1.25%. If we compare the brightness and peroxide consumption of DTPA- and HEDTA-pretreated pulp, the positive influence of HEDTA on TMP bleaching is obvious. The reason for the improved efficiency of HEDTA over DTPA is



7. Effect of chelating agents on TMP bleaching



8. Effect of chelating agents on peroxide consumption

Pretreatment/ Bleaching	ISO Brightness, %[a]	b* Value	Peroxide consumed, %[b]
DTPA/DTPA	71.5 ±0.2	11.5 ±0.1	75
EDTA/DTPMPA	72.9 ±0.3	11.3 ±0.2	65
DTPMPA/DTPMPA	73.0 ±0.2	11.5 ±0.2	67
HEDTA/DTPMPA	73.9 ±0.2	10.8 ±0.1	60

[a] After 2% hydrogen peroxide bleaching.
[b] Experimental error based on repetition is between 3% and 5% on the data reported.

IV. Effect of chelating agents on bleaching of TMP

not clear. However, HEDTA seems to have some chelation effect on copper. The metal profile of DTPA- and HEDTA- pretreated pulps did not significantly differ within the experimental precision. It is possible that even a small change in the Mn and/or Cu profile along the low concentration range would have a significant effect on the brightness and stability of pulp.

Addition of metal chelants to the bleach liquor for an HEDTA-pretreated pulp was not found to have an added advantage on brightness and peroxide consumption. However, the only exception was DTPMPA, where it helps decrease peroxide consumption to 1.19%.

To optimize the optical properties and the peroxide consumption, different combinations of sequestering agents at a concentration of 0.5% in the pretreatment and bleaching stages were tried. *Table IV* shows four combinations of chelating agents on the ISO brightness, the *b** coordinate, and peroxide consumption. These results show that using DTPMPA in the bleaching liquor, when bleaching a chelated pulp, is beneficial for all the properties described. The best combination among these three is when HEDTA is used at the chelation, yielding 73.9, 10.8, and 1.19% for ISO brightness, *b** coordinate, and peroxide consumption, respectively. This should be compared to the conventional DTPA/DTPA sequence, where values of 71.5, 11.5, and 1.49% are obtained for the same properties.

ECONOMIC ASPECTS

Replacing or substituting conventional sequestering agents with a suitable combination of two sequestrants can have major implications on the economics of the papermaking process. In spite of increasing the cost of sequestrants, major savings can be expected by reducing the peroxide consumption. The high cost of new chelants will be more than compensated by the reduced peroxide consumption and increased brightness gain. Laboratory data indicated that the residual peroxide can be increased by about 20% if HEDTA is used for pulp pretreatment, and a clear gain of 1.0–1.5 points can be achieved over DTPA-chelated pulp.

Again, incorporation of an additional 0.5% DTPMPA in the bleaching stage could increase residual peroxide by another 5–10%. Therefore, an overall minimum saving of about 20% in peroxide consumption can be achieved by a suitable combination of chelating agents and then by optimizing their sequence of addition in pretreatment and bleaching stages.

The increase in residual peroxide content allows cost savings in per-

KEYWORDS
Brightening, chelates, chelation, chemical degradation, hydrogen peroxide, manganese, peroxide bleaching, pH, pretreatment, thermomechanical pulps.

oxide consumption, which can be calculated as follows:

Savings = Cost x Amount x *R* x BPHD

where

Savings	=	savings per kg of paper
Cost	=	cost of hydrogen peroxide
Amount	=	amount of hydrogen peroxide used in bleaching
R	=	increase in residual hydrogen peroxide, %
BPHD	=	pulp bleached with HEDTA and DTPMPA sequence combination.

When 100% HEDTA–chelated and DTPMPA/peroxide–bleached pulp is used with 20% more residual hydrogen peroxide in a bleaching process with 2% peroxide at a cost of US$ 1.50/kg (100%), the cost reduction amounts to US$ 6.75/ton of paper produced from a single-stage bleaching process.

Cost savings due to brightness gain

Industrially, a gain of about 10 points can be achieved using DTPA-pretreated pulp at 1.5% peroxide consumption level. Therefore, an average additional 1.0–1.5 points brightness gain will save 10% additional peroxide. The costs saving due to brightness gain will then be an additional US$ 3.50/ton.

CONCLUSION

This study aims to optimize the pretreatment stage of high-yield pulps to maximize hydrogen peroxide bleaching efficiency. The study of the chelating efficiency of metal ions for several sequestering agents was made. The effect of the pretreatment conditions on the chelating efficiency of the agents was also examined. Bleaching trials followed to evaluate the effect of metal chelation on the bleaching efficiency of TMP by the measurement of ISO brightness and peroxide consumption.

Conditions such as temperature and retention time do not affect the chelation of manganese. Chelate concentration plays an important role and should be set at a maximum of 0.5% for all the chelants studied. pH is an important factor in sequestering metal ions. HEDTA is an excellent sequestering agent in acid media. Alkaline conditions favor chelation by DTPMPA.

Results from the hydrogen peroxide bleaching trials indicate that DTPA or DTPMPA should be added to the bleaching liquor to maximize bleaching efficiency of a nonchelated pulp. However, the addition of a sequestering agent is not necessary in bleaching an HEDTA-chelated TMP with the exception of DTPMPA, which slightly helps improve brightness and lower peroxide consumption. Finally, optimum results are obtained with an HEDTA pretreatment and by adding DTPMPA in the bleaching liquor, yielding 73.9%, 10.8, and 1.19% for ISO brightness, the b^* coordinate, and peroxide consumption, respectively. It is important to compare this chelant sequence to the most common DTPA/DTPA sequence, where results of 71.0%, 11.5, and 1.49% are obtained for the same properties. TJ

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