Refiner hydrogen peroxide bleaching of thermomechanical pulps

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ABSTRACT *The feasibility of the simultaneous pulping and bleaching of Norway spruce wood chips in the Kumagai Riki Kogyo (KRK) experimental pressurized laboratory refiner was investigated. Bleaches were made in both the primary and secondary stages of the TMP process. All experimental work was aimed at developing operating parameters for refiner bleaching that do not require the use of scale-forming sodium silicate.*

Secondary-stage refiner bleaching using diethylenetriamine pentamethylene phosphonic acid (DTPMP) as a peroxide stabilizer produced comparable brightness gains (10.40%) with methods simulating tower bleaching at a much shorter reaction time, thereby avoiding the use of sodium silicate and expensive bleaching towers.

KEYWORDS
Bleaching
Chelating agents
Hydrogen peroxide
Pulps
Refining

The recent importance placed on thermomechanical pulp (TMP) in the manufacture of not only newsprint but also papers of higher quality has proposed a need to increase TMP brightness (*1, 2*). At the same time, diversification of the primary materials, including sawmill scraps and wood with high bark content, has effected a general reduction in the brightness of unbleached TMP (*3, 4*). Consequently, efficient bleaching of TMP is important.

Of the two reagents generally used in lignin-retaining bleaching, hydrogen peroxide and sodium dithionite, the latter is the more economical brightening agent (*3*). Hydrogen peroxide is favored over sodium dithionite, however, because it can effect relatively large and more stable brightness gains. Peroxide bleaching is generally accomplished in a tower at a high pulp consistency (15–20%), with a relatively long reaction time (2–4 h). This technique leads to high capital costs because of the use of expensive and burdensome equipment.

The development of disc refiners capable of working at high consistency and under pressure in preparing TMP has generated the idea of refiner bleaching. The refiner is used as a high-speed mixer, and the reaction time is short. Thus, the overall process is simplified, and investment costs are reduced.

In this study, we examine the feasibility of simultaneously pulping and bleaching Norway spruce (*Picea abies*) wood chips in the KRK laboratory refiner. The results are compared with laboratory bleaches of the same pulps in polyethylene bags (bag bleaches). Since sodium silicate, a common peroxide stabilizing agent and weak buffer, coats refiner plates and quickly shortens their useful lifetimes, all experimental work was aimed at developing operating parameters for refiner bleaching without the use of sodium silicate.

Results and discussion

The study was focused on secondary-stage refiner bleaching at atmospheric pressure. Preliminary experimentation with pressurized, primary-stage refiner bleaching at higher temperatures had yielded results that were less than satisfactory. This primary-stage bleaching was successful only at high concentrations (4%) of hydrogen peroxide in the absence of sodium silicate and magnesium sulfate. Excessive peroxide decomposition under the higher temperature (135°C) may have been the cause of poor bleaching response.

Effect of chelating agents

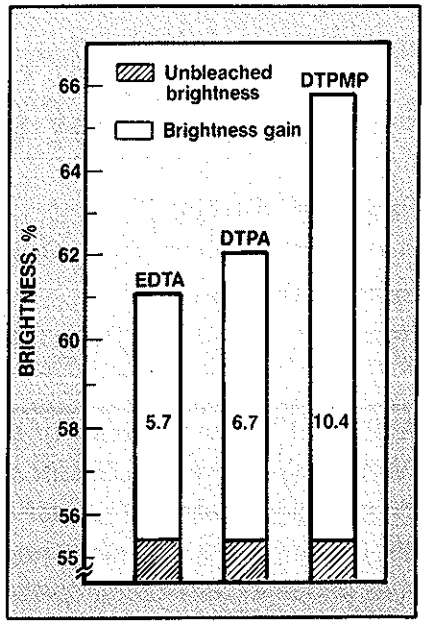
In an effort to replace sodium silicate, we examined the effects of DTPMP, diethylenetriaminepentaacetic acid (DTPA), and ethylenediaminetetraacetic acid (EDTA) in secondary-stage refiner bleaching. We did so by measuring the brightness and metal content of TMP prepared under the conditions listed in **Table I**. Before running the secondary refining stage, the primary-stage TMP was mixed with the bleaching agents. The peroxide stabilizing agent, sodium hydroxide, and hydrogen peroxide were hand kneaded, in that order, and were added as a solution at the desired pulp consistency.

I. Conditions for secondary-stage refiner bleaching

	EDTA	DTPA	DTPMP
Chelating agent,[a] %	0.29	0.5	0.57
NaOH, %	2.0	1.2	2.4
Initial pH	11.5	11.3	11.3
Final pH	9.9	9.6	9.3
Residual H_2O_2, %	8	8	36

[a] 1.24 mmol.
Secondary stage: 1% H_2O_2, 50°C, 12% consistency, 0.60–0.70 mm of plate clearance.
Primary stage: 55.5% brightness, 0.33 mm of plate clearance, 1 min of presteaming, 135°C.

1. The effect of chelating agents in secondary-stage refiner bleaching (1% H_2O_2, 1.24 mmol chelating agent, 12% consistency, 50°C)



II. Effect of chelating agents on the brightness and transition metal content of bleached pulps

	Unbleached	EDTA	DTPA	DTPMP
Brightness, %	55.4	61.1	62.1	65.8
Brightness gain, % points	...	5.7	6.7	10.4
Iron, ppm	162	101	56	66
Copper, ppm	30	22	12	7
Manganese, ppm	58	7	2	6

Adding EDTA, DTPA, and DTPMP in equimolar proportions resulted in brightness gains of 5.7, 6.7, and 10.4 percentage points, respectively (**Fig. 1**). Thus, DTPMP provided the greatest brightness improvement, giving a value of 65.8%. These results are in agreement with those of Kowalski (*5*), who found that DTPMP was more effective as a peroxide stabilizer than DTPA because of its greater stability toward oxidation during peroxide bleaching. In turn, DTPA was more effective than EDTA because the magnitudes of the stability constants for Fe (III), Cu (II), and Mn (II) are greater for DTPA.

The improvement in bleaching gained by the addition of chelating agents can be roughly correlated with the degree of metal removal from the pulp (**Table II**). The general order of efficiency of the chelating agents in removing transition metals was DTPMP ≅ DTPA > EDTA. The DTPMP addition removed 59% of the iron, 77% of the copper, and 90% of the manganese in the unbleached secondary-stage pulp. The less-effective EDTA removed only 38% of the iron, 27% of the copper, and 88% of the manganese.

The effectiveness of DTPMP was also studied by adding varying amounts to a series of secondary-stage refiner bleaches. The effectiveness of DTPMP decreased dramatically at charges greater than 0.28% (0.62 mmol), as illustrated in **Fig. 2**. Apparently, at 0.62 mmol the DTPMP had chelated most of the metals present and a "ceiling" effect was observed in the bleachability with additional chelator.

III. Conditions for secondary-stage refiner bleaching with recycled liquor

	Fresh liquor	Recycled	Re-recycled
NaOH, %	2.40	1.92	1.92
Initial pH	11.4	11.3	11.3
Final pH	9.6	9.5	9.4
Residual H_2O_2, %	22	19	20

IV. Brightness and transition metal content in bleaching with recycled liquors

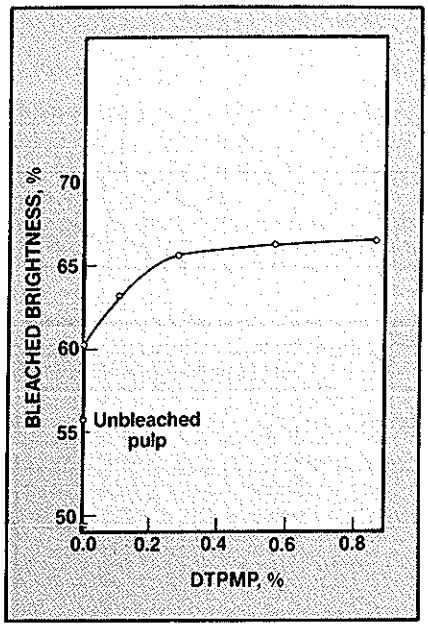
		Unbleached				
Pulp	Wood-meal	Primary stage	Secondary stage	Fresh liquor	Recycled	Re-recycled
Brightness, %	...	55.5	55.4	65.4	65.3	65.4
Brightness gain, % points	...	...	...	10.0	9.9	10.0
Iron, ppm	9	27	162	132	76	56
Copper, ppm	<1	4	30	27	7	5
Manganese, ppm	85	62	58	11	11	6

Recycling of bleach liquor

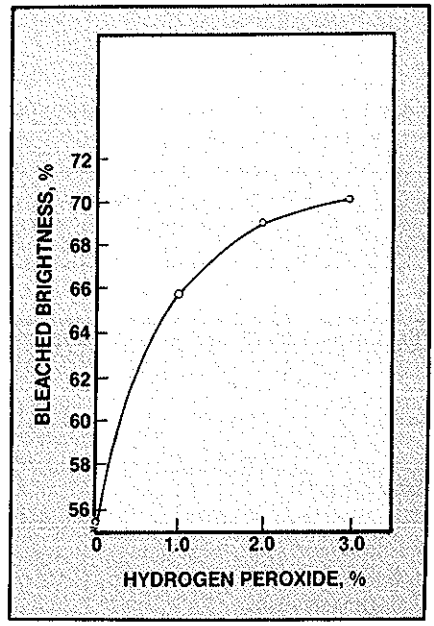
Because of high levels of hydrogen peroxide residual (~23–36%) in some bleaches, the recycling of peroxide bleach liquors was examined. After bleaching one pulp (**Table III**) with fresh liquor, the liquor was pressed out on a Buchner funnel under vacuum and was titrated for residual peroxide. Additional peroxide was then added to bring the concentration to 1%, and 0.5% DTPMP was added with sufficient sodium hydroxide to raise the pH to 11.3. After bleaching a new pulp sample with the recycled, fortified liquor, the procedure was repeated by recycling and fortifying the previously cycled liquor and bleaching another new pulp sample.

Recycling and fortifying the bleach liquors produced the same brightness

2. The effect of DTPMP addition in secondary-stage refiner bleaching (1% H_2O_2, 1.2-3.2% NaOH for an initial pH of 11.3, 12% consistency, 50°C)



3. The effect of hydrogen peroxide charge in secondary-stage refiner bleaching



V. Effect of the hydrogen peroxide charge in secondary-stage refiner bleaching

H_2O_2, %	1.0	2.0	3.0
Brightness, %	65.8	69.0	70.1
Brightness gain, % points	10.4	13.6	14.7
NaOH, %	2.4	3.0	3.6
Final pH	9.3	9.6	9.7
Residual H_2O_2, %	36	38	41

0.57% DTPMP, 50°C, 12% consistency, initial pH 11.3.
Primary stage conditions as described in Table I.

VI. Effect of consistency in secondary-stage refiner bleaching

Consistency, %	8	10	12
Brightness, %	64.5	64.8	64.8
Final pH	9.7	9.6	9.5
Residual H_2O_2, %	36	27	21

1% H_2O_2, 0.3% DTPA, 1.35% NaOH, 50°C, initial pH 11.2

gains (10 percentage points) as with the bleach using fresh liquor (**Table IV**). Under these conditions, recycling of fortified bleach liquor may be employed to reduce chemical costs.

Recycling and fortifying the bleach liquors in secondary-stage refiner bleaching removed increasing amounts of transition metals in each application (**Table IV**) and increased the effectiveness of DTPMP. This resulted from the addition of an additional 0.57% DTPMP to each fortified liquor.

Effect of the hydrogen peroxide charge

The amount of hydrogen peroxide was varied in increments of 1.0% up to a total of 3.0% while holding other refining variables constant, with the exception of sodium hydroxide, which was varied to give the same initial pH (11.3) for each bleach. Secondary-stage refiner bleaching was performed under the conditions listed in Table I and **Table V**. For 1%, 2%, and 3% peroxide applications, the bleached brightness values were 65.8%, 69.0%, and 70.1% respectively, which represent brightness gains of 10.4, 13.6, and 14.7 percentage points (Table V).

The slope of the curve in **Fig. 3** indicates that the peroxide becomes less effective at applications over 1% and that leveling off occurs at 3%. This brightness ceiling effect has also been observed in conventional tower bleaching.

Effect of refiner variables

Consistency. The effect of consistency was examined in the 8-18% range while holding other variables constant (**Table VI**). In the workable range of consistency (8-12%), the refiner acted as an excellent mixer and provided a uniform brightening response with a relatively insignificant effect on bleached brightness.

At 15% and 18% consistency, the pulp burned because of the high alkalinity of the slurry and the increased retention time resulting from the low feed rate. For this reason, the high consistency levels of tower bleaching could not be attained. The residual peroxide decreased with increasing consistency, presumably because the greater effective metal concentration caused a greater amount of peroxide decomposition.

Temperature. Increasing the refining temperature from 50° to 80°C while bleaching in the presence of DTPMP had little effect on brightness. From different sets of experiments using both DTPMP and DTPA, we found that 50°C was the best temperature for bleaching.

Feed rate. The effect of pulp feed rate on brightness during secondary-stage refiner bleaching was monitored while other variables were held constant. A low feed rate, which allowed a somewhat longer residence time, resulted in slightly better mixing, as evident from an increase in brightness of 1.0 percentage point.

However, increasing the retention time further had little effect on brightness. These results are in agreement with those of Solinas (*6*), who claimed that only a relatively short retention time is necessary for secondary-stage refiner bleaching to obtain optimum brightening response.

Plate clearance. Changing the plate clearance in the range of 0.55-0.70 mm while keeping other parameters constant also had little effect on the bleached brightness. The

throughput decreased only 5% as the clearance decreased from 0.70 mm to 0.55 mm; therefore, the residence time was not increased sufficiently to increase the bleaching response.

Physical properties

Secondary-stage refiner bleaching increased the tear index about 5% and 10% for applications of hydrogen peroxide of 1% and 3%, respectively (**Table VII**). A 10% increase in the tensile index was observed at 3% hydrogen peroxide, while little change occurred at 1%. The burst index was essentially unchanged. The scattering coefficient increased, and the absorption coefficient decreased with increasing peroxide, indicative of the bleaching effect of the peroxide. The TAPPI opacity decreased approximately 4% at 1% and 3% hydrogen peroxide.

VII. Physical properties of secondary-stage refiner bleached pulps

CSF, mL	76.0	82.0	91.0
H_2O_2, %	0.0	1.0	3.0
Apparent density, g/cm³	0.390	0.381	0.389
Burst index, kPa·m²/g	1.21	1.15	1.24
Tear index, mN·m²/g	5.57	5.81	6.08
Tensile index, N·m/g	28.1	27.9	30.8
Light scattering coefficient, m²/kg	47.1	47.4	52.5
Light absorption coefficient, m²/kg	4.74	2.35	1.76
TAPPI opacity, %	91.4	88.0	88.3

0.57% DTPMP, 50°C, 12% consistency

Comparison with laboratory bag-bleaching

In comparing secondary-stage refiner bleaching and laboratory bag-bleaching using 1% peroxide and DTPMP as a chelating agent, the same primary-stage pulp (Table I) was used to produce the secondary-stage pulp for both types of bleaching. As shown in **Table VIII**, secondary-stage refiner bleached pulp had a bleached brightness of 65.8%, representing a brightness gain of 10.4%. By comparison, the bag-bleached pulp bleached in water from the refiner had a bleached brightness of 67.8% and a brightness gain of 12.4%.

Thus, secondary-stage refiner bleaching with DTPMP as chelant achieved 84% of the brightness gain achievable by bag bleaching. Additionally, the brightness value of the bag-bleached pulp using distilled water was about 1.0% higher than that of the bag-bleached pulp using water from the refiner system. The higher brightness values obtained in the bag-bleached pulps were possible in part because of the sodium silicate and magnesium sulfate used as peroxide stabilizing agents.

Solinas (*6*) and Loras (*1*) obtained brightness gains during secondary-stage refiner bleaching that were generally equivalent to those obtained using conventional methods simulating retention tower brightening. However, they used sodium silicate and magnesium sulfate in their refiner bleaching.

The results in Table VIII show that the total quantity of transition metals sorbed on the secondary-stage refiner bleached pulp was smaller than the amount sorbed on the bag-bleached pulps. Consequently, DTPMP chelated the free transition metals more effectively as they were generated during secondary-stage TMP manufacture, as opposed to the removal of already strongly bonded metals present in manufactured secondary-stage pulp through pretreatment with the same chelating agent.

VIII. Comparison of refiner and bag-bleached pulps

		Bag-bleached pulps[b]	
Sample	*Refiner bleached pulp*[a]	*Refiner water*	*Distilled water*
Brightness, %	65.8	67.8	68.6
Brightness gain, % points	10.4	12.4	13.2
Iron, ppm	66	140	117
Copper, ppm	7	18	13
Manganese, ppm	6	2	2

[a]Refer to Table V for conditions.
[b]Pretreated with 0.57% DTPMP (pH 10.5, 2% consistency, 30 min at room temperature); 1% H_2O_2, 0.05% $MgSO_4 \cdot 7H_2O$, 5% Na_2SiO_3, 1.25% NaOH (pH 10.9), 12% consistency, 50°C, 1 h.

Summary

Secondary-stage hydrogen peroxide refiner bleaching in a laboratory refiner using DTPMP as a peroxide stabilizer produced, in a much shorter reaction time, brightness gains (10.4 percentage points) comparable with those obtained using methods simulating tower bleaching. These results indicate that expensive bleaching towers and the use of scale-forming sodium silicate may be avoided. The brightness gain was 84% of that obtained in a bag bleach.

Recycling of fortified bleach liquor was effectively employed, indicating the potential for reducing chemical costs. By adding DTPMP to the fortified liquor, increasing amounts of transition metals were removed in each application.

The chelation of metals is essential for maximum bleaching efficiency to be achieved. The improvement in bleachability and the efficiency in removing metals by adding chelating agents to secondary-stage refiner bleaching in general was of the order DTPMP≅DTPA>EDTA.

A modest increase in strength properties was observed at 3% peroxide, with essentially no increase at 1% peroxide. The tear and tensile indexes increased about 10%, and the burst index remained unchanged.

Among several refiner variables, a low feed rate through the refiner during bleaching produced a small increase in bleached brightness. Varying refiner consistency (8-12%) had little effect. Increasing bleaching temperature from 50°C to 80°C had essentially no effect on final bleached brightness.

Using the refiner as a high-speed mixer simplifies the bleaching process. Hydrogen peroxide refiner bleaching of thermomechanical pulps is a possible alternative to tower bleaching and has great potential in reducing capital costs.

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