Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES

[redacted]

NUMBER 409

AN EVALUATION OF SODIUM CARBONATE AS A REPLACEMENT FOR SODIUM HYDROXIDE IN HYDROGEN PEROXIDE BLEACHING OF CTMP

A.W. RUDIE, T.J. MCDONOUGH, ET AL.

DECEMBER, 1991

An Evaluation of Sodium Carbonate as a Replacement for Sodium Hydroxide in Hydrogen Peroxide Bleaching of CTMP

A.W. Rudie, T.J. McDonough, et al.

Submitted for presentation at
CPPA Annual Meeting
January 28, 1992
Montreal, Canada

For Members Only

AN EVALUATION OF SODIUM CARBONATE AS A REPLACEMENT FOR SODIUM HYDROXIDE IN HYDROGEN PEROXIDE BLEACHING OF CTMP

A. W. Rudie and T. J. McDonough
Inst. of Paper Sci. and Tech.
Atlanta, GA 30318

F. Rauh, R. J. Klein, and J. L. Parker
FMC Corporation
Princeton, NJ 08543

S. A. Heimburger
FMC Canada Inc.
Vancouver, BC V6C 1N5

Abstract: A series of experiments was performed to evaluate the effect of substituting sodium carbonate (soda ash) for the sodium hydroxide used in peroxide bleaching of spruce CTMP. Three peroxide levels were tested: 1, 2, and 4% H_2O_2 (OD basis) and two levels of caustic substitution, 50% and 80%. At both the 2% and 4% peroxide levels, substituting 50% of the caustic charge with soda ash decreased the initial brightness gain by 1 point in TAPPI brightness. At the 80% caustic substitution level, the brightness gain decreased 1.5 points. Use of sodium carbonate as part of the alkali source in the bleaching process reduces the sensitivity of final bleached brightness to the alkali charge and should result in improved control. In all cases, soda ash substitution was found to improve brightness stability, and in some cases, ash substituted samples gave higher reverted brightness than the caustic control. A mathematical model was developed to describe peroxide bleaching with both sodium hydroxide and sodium carbonate as sources of alkali. Handsheets were made from selected pulp samples. Tear Index and Burst Index were unaffected by ash substitution. Tensile Index was reduced 5 to 15%.

Résumé: Une série d'expérience fut effectuée afin d'évaluer l'effet de la substitution de l'hydroxyde de sodium (soude caustique) par le carbonate de soude dans le blanchiment au péroxyde d'hydrogéne de la pâte PTCM (épinette). Trois niveaux de dosage de péroxyde furent analysés: 1, 2 et 4% H_2O_2 (base anhydre) et deux niveaux de substitution de soude caustique, soit 50 et 80%. Au deux niveaux de 2 et 4% de péroxyde et en remplaçant 50% de la charge de soude caustique par le carbonate de soude, le degré de blancheur initiale fut réduit de 1 point (échelle de TAPPI). En remplaçant la soude à 80%, le degré de blancheur fut réduit de 1.5 point. L'utilisation du carbonate de soude comme portion de la source d'alcali dans le procédé de blanchiment réduit la sensibilité du degré de blancheur finale à la charge d'alcali et devrait conduire à une amélioration du contrôle. Dans tous les cas, la stabilité du degré de blancheur fut améliorée par la subtitution du carbonate de soude et dans quelques cas, les échantillons avec le remplacement par le carbonate de soude ont produit des degrés de blancheur plus élevés aprés réversion que ceux obtenus de l'échantillon de contrôle avec la soude caustique. Un modéle mathématique fut développé afin de décrire le blanchiment au péroxyde d'hydrogéne avec la soude caustique et le carbonate de soude comme sources d'alcali. Des formettes furent fabriquées à partir d'échantillons sélectionnés de pâte. Les indices de déchirement et d'éclatement ne subirent aucun changement suite à la substitution au carbonate de soude. L'indice de rupture fut réduit de 5 à 15%.

INTRODUCTION

Peroxide bleaching of high-yield pulps has traditionally been conducted under alkaline conditions using a mixture of sodium hydroxide and sodium silicate to raise the pH and activate peroxide and lignin for effective bleaching.[1,2] Recent increases in the price and concerns over the continued availability of caustic have lead to a renewed interest in alternative sources of alkali for peroxide bleaching.

It is well-known that for a given pulp and peroxide charge, there is an optimum alkali charge that will produce the highest achievable brightness gain.[2,3] At charges below optimum, the bleaching process is slow, and there is insufficient alkali to drive the peroxide bleach reactions to completion. A high alkali charge increases the rate of the peroxide decomposition reactions, giving poor peroxide utilization. Furthermorè, in a process with a fixed retention time, too much caustic leads to complete consumption of peroxide and an increase in alkaline reactions that reduce brightness.[1,4]

Silicate performs a dual role in the process as a peroxide stabilizer and as an alkaline buffer.[1,5] Adding caustic at the end of a conventional peroxide bleach stage can make use of the residual peroxide for additional brightness gains.[6] This suggests that there may be benefits in increasing the buffering capacity in the peroxide bleach process beyond that commonly obtained with silicate.

Sodium carbonate is recognized throughout the chemical industry as an alternative source of alkali for many processes. It has attracted attention in the paper industry for applications in refiner bleaching[7] and as a replacement for sodium hydroxide in oxygen bleaching[8], alkaline extraction[9], and as a sodium source in the kraft and sulfite pulping processes. Recently, it has been examined as an alkali source in peroxide bleaching of TMP.[10] The present research has investigated the efficiency of sodium carbonate as a partial replacement for caustic in peroxide bleaching of CTMP. The effects of the sodium carbonate substitution on development of pulp strength in peroxide bleaching and on the brightness stability of the bleached pulps are also reported.

RESULTS AND DISCUSSION

A commercial spruce CTMP was pretreated with 0.2% DTPA and dewatered to 25% consistency in preparation for peroxide bleaching. A series of conventional hydrogen peroxide bleaching experiments was conducted to determine the effect of the sodium hydroxide charge on final brightness. Once the caustic charge required to maximize brightness had been identified, it was reduced by 50% and 80% and sodium carbonate added to determine the brightness response with the mixed alkali. Summary results are reported in Table I. Complete experimental results are listed in Table IV and Table V following the report.

In both the 2% and 4% peroxide cases, replacement of 50% of the ideal sodium hydroxide charge with sodium carbonate results in a loss of approximately 1 point in brightness. Replacement of 80% of the caustic increases the brightness loss to 1.5 points.

A mathematical model was developed to predict brightness gain. Using a parameter fitting approach, coefficients were determined to fit the data to an equation for a parabola. The resulting equation is listed below.

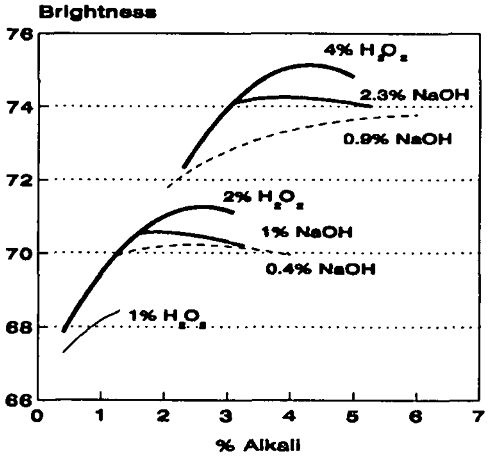

Figure 1. Model results for soda ash substitution. Alkali is the sum of the sodium hydroxide and sodium carbonate charges and does not include silicate. Starting brightness is 61 GE.

This equation has been used to prepare the summary plot in Figure 1 and the contour plots of brightness gain for the 4% (Figure 2) and 2% (Figure 3) hydrogen peroxide cases. Figure 1 demonstrates the reduced sensitivity of the bleaching response to alkali charge when sodium carbonate is used to replace some of the sodium hydroxide normally used in peroxide bleaching.

When using 4% peroxide, the maximum brightness gain is 14.5 points GE, obtained with 4.4% sodium hydroxide on OD pulp (Figure 2). The maximum brightness is obtained with sodium hydroxide as the only source of alkali. Under alkali deficient conditions, i.e., 2% sodium hydroxide charge, the initial effect of adding sodium carbonate is to fortify the alkali charge and increase the brightness gain, in this case from ≈ 11 points to 13 points GE. The slopes of the *iso*brightness lines represent the soda ash to caustic substitution ratios. In the alkali deficient region, this is about 1.8 parts carbonate to replace 1 part caustic. In the excess caustic region, the replacement ratio is quite variable, ranging from 0.7 to 1 in the high brightness gain region to ≈ 3 to 1 carbonate to caustic for the 10 point *iso*brightness line.

$$\begin{aligned}BRIGHTNESS = 61.1 &+ 6.56(H_2O_2)^{0.42} - 0.5(0.6 + H_2O_2\\ &- 1.18NaOH - 1.6\sqrt{Na_2CO_3})^2\\ &+ 0.57NaOH + 0.08Na_2CO_3\end{aligned}$$

$$R^2 = 0.94,\ SE = 0.87$$

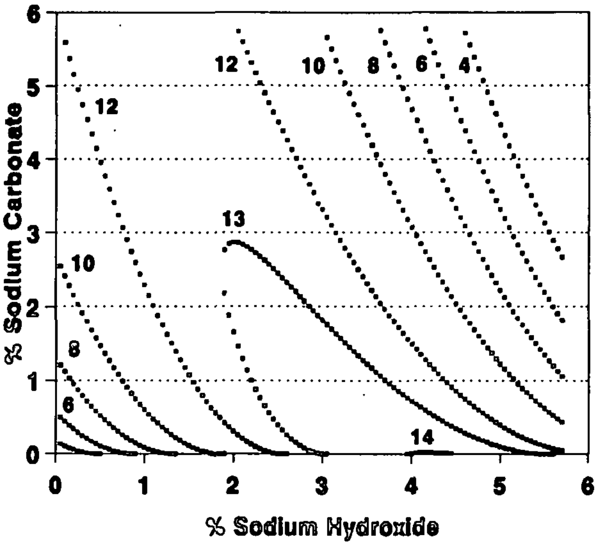

Figure 2. Contours of constant estimated brightness gain when using 4% peroxide and mixtures of sodium hydroxide and sodium carbonate.

The brightness gain contour plot for 2% peroxide (Figure 3) is very similar. Maximum brightness is achieved with the addition of 2.5% sodium hydroxide as the source of alkali. In the caustic deficient region, sodium carbonate increases brightness gain with a substitution ratio of approximately 1 to 1. In the excess alkali region, added carbonate decreases brightness with a substitution ratio, ranging from 0.5 to 1 to 2 to 1.

Evaluation of Residuals

Peroxide and alkali residuals are listed in Tables IV and V. For the caustic control cases, the alkali charge required to maximize brightness is slightly lower at the longer retention times. At maximum brightness, the final pH is lower, the strong base residual smaller, and the peroxide residual 20% larger when using sodium carbonate to supplement the caustic charge. In both the caustic and soda ash cases, the residual peroxide decreases linearly with increasing total alkali charge. The high peroxide residual in the carbonate substitution cases might be effectively utilized in a two-stage peroxide bleaching process that either recycles the residual peroxide to the first stage or reactivates the residual peroxide with a

Table I. Alkali charges at maximum brightness for the 90-minute retention time.

H_2O_2 %	NaOH %	Na_2CO_3 %	Brightness GE
2.0	2.5	-	71.8
2.0	1.0	1.3	70.6
2.0	0.4	3.2	70.3
4.0	4.0	-	75.6
4.0	2.3	1.3	74.8
4.0	0.9	4.9	74.2

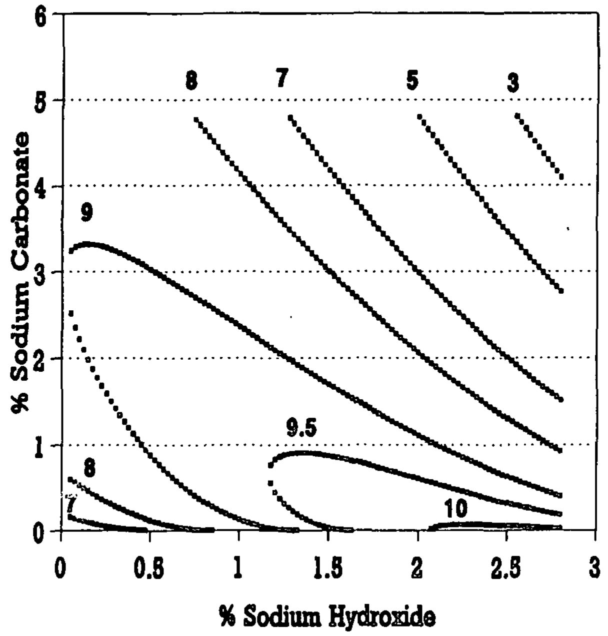

Figure 3. Contours of constant brightness gain using 2% peroxide and mixtures of sodium hydroxide and sodium carbonate.

second charge of alkali as proposed by Lachenal.[6]

Handsheet and Physical Properties

Selected samples at or near the optimum alkali charge were made into handsheets and tested for tensile, tear, and burst strength. Results of these tests are reported in Table II. There is a slight loss in tensile index when substituting carbonate for sodium hydroxide as the bleaching alkali. This is most pronounced at the 2% hydrogen peroxide level where the tensile index has been reduced by 15%. At 4% hydrogen peroxide on pulp, the loss is only about 5%. Tear index and burst index are not significantly affected by the change in alkali.

Table II. Handsheet test results on spruce CTMP bleached with hydrogen peroxide and sodium hydroxide and sodium carbonate as alkali. Results are for samples at or near the optimum alkali charge.

H_2O_2 %	NaOH %	Na_2CO_3 %	Tensile Index N·m/g	Tear Index mN·m²/g	Burst Index kPa·m²/g
2.0	2.5	-	17.5	6.3	0.66
2.0	1.0	1.3	15.2	5.9	0.66
2.0	0.4	3.2	15.1	5.8	0.63
4.0	4.0	-	20.2	7.6	0.88
4.0	2.3	3.0	19.2	7.8	0.84
4.0	0.94	4.9	19.7	7.6	0.83

The loss in tensile index in the samples bleached with sodium carbonate as alkali is probably a result of reduced alkaline swelling and formation of fewer carboxylic acid functional groups with the milder alkali.[11] The more pronounced effect on tensile strength at 2% than at 4% peroxide has been observed by Moldenius.[12] The relative insensitivity of tear strength to peroxide and alkali is also reported by Moldenius.

Brightness Reversion

Reverted brightness was measured on several handsheets after six and nine months of storage in an office environment. During the majority of this time, the samples were in a file drawer shielded from light. After nine months of storage, the samples were exposed to 1 hour of intense light in an Oriel Solar Simulator. Reverted brightness results are reported in Table III.

Average brightness loss after nine months storage is 2.2 points for the samples bleached with a mixture of sodium carbonate and sodium hydroxide. This compares to an average brightness loss of 4.5 points for the samples bleached with 100% sodium hydroxide. After reversion, the samples bleached with 2% peroxide and mixed alkali exceed the brightness of the sodium hydroxide control.

At the 4% peroxide bleach level, the brightness difference between the sodium hydroxide control and samples with carbonate substitution has narrowed from the original 2.5 points GE to about 1.5 points GE after reversion.

The brightness loss results appear to be sensitive to the carbonate substitution level, averaging 12.6 points loss with 100% sodium hydroxide, 11.3 points loss at 50%

Table III. Initial brightness and ambient and light reverted brightness results for samples bleached at optimum alkali charge. The 4% peroxide data is for bleaches conducted with a 3-hour retention time.

NaOH %	Na_2CO_3 %	Brightness Initial	6 mo. (dark)	9 mo. (dark)	Light reverted
2% H_2O_2					
22.5.0	-	72.6	67.6	66.8	60.2
2.01.0	1.32	71.4	70.5	69.4	61.3
2.00.4	/3.2	70.2	68.8	68.0	60.5
4% H_2O_2					
4.04.0	-	77.5	75.1	74.3	64.7
4.02.3	3.0	75.2	73.8	72.9	62.6
4.00.9	7.4	74.1	72.7	71.8	63.6

carbonate substitution, and 10.1 points loss at 80% carbonate substitution.

The susceptibility to reversion may be dependent on the final pH of the bleach solution. *Ortho*-quinones have been detected in light reverted mechanical pulps, and the catechol, *ortho*-quinone redox couple is implicated as a major contributor to brightness reversion in high-yield pulps.[13] Hydroquinones are stable to peroxide under some bleaching conditions and, in fact, can be synthesized by the peroxide oxidation of acetoguaiacol and other suitable α-ketone precursors in the Dakin reaction.[14]

The stability of the hydroquinone may depend on the final pH. Above pH 10, hydroquinones and catechols are detected[15] as products of model compound oxidations with hydrogen peroxide. At pH 9, they readily react with peroxide,[16] and they are rarely observed as products of model compound experiments conducted at low pH or without excess caustic. Hocking has recorded the effect of different sources of alkali on conversion of *p*-hydroxyacetophenone to hydroquinone.[17] Under conditions that give a final pH under 10, Hocking observes a lower yield of hydroquinone relative to the amount of *p*-hydroxyacetophenone consumed in the reaction, consistent with an increase in decomposition of the hydroquinone.

The failure to maintain brightness when adding sodium carbonate is not fully understood. It is clear that the weaker base and buffering effect of sodium carbonate changes the pH profile of the conventional peroxide bleach. It may be that a higher initial pH obtained with sodium hydroxide promotes reactions between lignin and peroxide that are slow at the lower starting pH expected with sodium carbonate. It has also been shown that peroxide bleach efficiency is sensitive to the rate of decline in pH, as well as, the starting pH.[4] It is not possible to rule out these effects without additional experiments using other buffers.

Catechol oxidation to *o*-quinones at low residual pH adds another plausible explanation. Quinones react readily in alkali to give colored condensation products that are difficult to remove by further bleaching.[7b] If the lower final pH of the sodium carbonate experiments results in increased oxidation of catechols to *o*-quinones, the resulting condensation products could lead to a lower final brightness, while the reduction in catechols should improve the brightness stability as observed in these experiments.

A fourth possibility is a change in peroxide reactivity due to the formation of an addition complex between peroxide and carbonate. Although sodium carbonate peroxyhydrates are well-known, they hydrolyse rapidly, and the reactivity generally follows that of hydrogen peroxide.[18] However, formation of peroxycarbonates will reduce the effective concentration of hydrogen peroxide and the peroxy anion. This would result in a slower reaction rate and slower bleaching. The change in optimum pH can be either a pH sensitivity in the equilibrium for formation of the peroxycarbonate or participation of peroxycarbonate in bleaching at the lower pH. Since the optimum pH for bleaching high-yield pulps with peroxyacetic acid is around pH 8.5[19], the second of the two is a distinct possibility. It is also possible that the carbonate anion stabilizes the free radicals implicated in peroxide bleaching.[20]

Several follow-up experiments were carried out in an attempt to evaluate some of these hypotheses. Split alkali addition with sodium hydroxide added with the peroxide and sodium carbonate added 30 minutes later failed to increase the brightness to the caustic control levels. Decreasing the silicate charge by 50% or increasing the temperature to 70° C also failed to increase the brightness gain.

CONCLUSIONS

Based on the experimental work and the preceding discussions, the following conclusions can be drawn:

- Sodium carbonate can be successfully substituted for up to 80% of the sodium hydroxide required in peroxide bleaching of spruce CTMP. Although the optimum ratio for replacing sodium hydroxide with sodium carbonate is sensitive to the pulp, bleaching conditions, and peroxide charge, it generally appears to be close to a normalized basis, i.e., 1.3 g of soda ash to each gram of caustic.

- Sodium carbonate added as a partial replacement for the caustic normally used in peroxide bleaching decreases the sensitivity of the bleaching process to the alkali charge and may improve control of the final brightness.

Use of sodium carbonate to replace part of the caustic required in peroxide bleaching will result in a slight loss in brightness gain, on the order of 1 to 1.5 points in TAPPI brightness.

Spruce CTMP bleached with sodium carbonate as part of the alkali charge exhibits improved brightness stability relative to conventionally bleached pulps using sodium hydroxide and sodium silicate as the only sources of alkali.

Peroxide bleaching with mixtures of sodium hydroxide and sodium carbonate results in a 5 to 15% loss in tensile strength relative to controls bleached using 100% caustic.

There is no significant change in either tear index or burst index when using sodium carbonate to replace up to 80% of the caustic requirements in peroxide bleaching.

Experimental Procedures

Hydrogen peroxide (30-35% Fisher technical grade) was diluted with distilled water to ≈ 5% peroxide and titrated periodically to determine strength. Sodium hydroxide (Mallinckrodt analytical grade anhydrous pellets) was dissolved in distilled water to a nominal solution strength of 10%, with actual strength determined by titration. Sodium silicate (Fisher Technical Grade 40 to 42 Bé), Magnesium sulfate heptahydrate (Mallinckrodt analytical reagent) and Diethylenetriamine-pentaaceticacid (DTPA) (Aldrich Chemical Company, *penta*acid form) were used as is.

A large sample of unbleached spruce CTMP was obtained from a mill in Canada and stored at 5° C until needed. Before bleaching, samples were diluted to 4% consistency and treated with 0.2% DTPA at 50° C for 30 minutes. The samples were then dewatered on a büchner funnel and centrifuged to 25% consistency or higher. The batches were recombined and blended to provide a uniform starting pulp for the experiments. A bleach liquor consisting of 3% (1.5 g) sodium silicate, 0.05% (0.025 g) magnesium sulfate (anhydrous basis), and appropriate amounts of sodium hydroxide and sodium carbonate were mixed in enough distilled water to reduce a 50 OD gram sample[21] of pulp to 20% consistency. After everything dissolved, the desired amount of hydrogen peroxide was added to the bleach liquor and the entire solution mixed with pulp in a Hobart® mixer. The sample was stirred for 10 minutes, transferred to a plastic bag, sealed, and placed in a water bath set at 60° C.

The bag remained in the constant temperature water bath for 90 minutes at which time it was opened and a filtrate sample obtained and titrated for residual peroxide[22], sodium hydroxide, sodium carbonate (pH 8.3), and sodium bicarbonate (pH 3.8).[23] The residual alkali generally behaved in titration as a mixture of sodium carbonate and sodium bicarbonate (i.e., the molar concentration of base in the pH 8.8 to pH 3.8 part of the titration exceeded the molar concentration of base in the first part of the titration). To conform with standard practice, the residual hydroxide and carbonate are reported as sodium hydroxide % on OD pulp rather than the analytically correct sodium carbonate. The bicarbonate is reported as sodium bicarbonate % on OD pulp.

The pulp was neutralized to pH ≈ 7 and handsheets formed for brightness testing (TAPPI T-218 and T-452). In some experiments using 4% peroxide, samples were taken for brightness determination at both 90 minutes and 3 hours retention times to determine if the longer retention period favored carbonate addition. Where this information is available, it is reported in Table 5. Near the end of the study, the sample size was reduced to 25g OD to conserve pulp. With the smaller sample size, it was not possible to obtain the chemical residuals on both the 90-minute and 3-hour samples. In these cases the 3-hour data was collected, and the 90-minute data is not available.

Starting pulp was sampled four times during the course of the experiments. The brightness varied from a low of 60.7 to a high of 62.0, and the changes were not correlated with time. Of the 49 data records listed, 11 are replicates (including the four unbleached controls). Average deviation from the mean for all replicated data is ±0.34 points GE brightness, with a standard deviation of 0.45.

Ambient brightness reversion was evaluated by placing the samples in plastic bags and loading them into a standard 10" X 13" interoffice envelope. The envelope was then placed in a file drawer for storage. Brightness was tested after six months and nine months of storage.

Light reverted brightness measurements were conducted on the nine-month reverted samples. The brightness tabs cut from the handsheets were clamped at a distance of 10.5" from the lens of an Oriel 1000 Watt Solar Simulator. The Solar Simulator uses a Xenon arc lamp to simulate the solar spectrum and was fitted with an air mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. An exhaust fan provided air circulation to minimize heating of the sample. Each sample was exposed for one hour. Samples were then stored for 24 hours to allow the brightness to stabilize[24] before submitting for the brightness measurement.

Regression analysis and model development were carried out using Statistical Graphics Corporation Statgraphics® 3.0.

REFERENCES

1. STRUNK, W. G., "Factors Affecting Hydrogen Peroxide Bleaching for High-Brightness TMP", *Pulp and Paper* 54(6): 156(1980).

2. REICHERT, J. S. and PETE, R. H., "Peroxide Bleaching of Groundwood", *TAPPI J.* 32(3): 97(1949).

3. MOLDENIUS, S., "The Stoichiometry of Peroxide Bleaching of Mechanical Pulps", *Svensk Papperstidning* 85(15): R116(1982).

4. COLODETTE, J., FAIRBANK, M. G., and WHITING, P., "The Effect of pH Control on Peroxide Brightening of Stonegroundwood Pulp", *J. Pulp and Paper Sci.* 16(2): J53(1990).

5. ALI, T., McARTHUR, D., STOTT, D., FAIRBANK, M., and WHITING, P., "The Role of Silicate in Peroxide Bleaching of Mechanical Pulp. 1. The Effects of Alkalinity, pH, Pre-Treatment with Chelating Agent and Consistency", *J. Pulp and Paper Science* 12(6): J166 (1986).

6. LACHENAL, D., BOURSON, L., and DUBREUIL, M., "Reactivation of Residual H_2O_2 in High Yield Pulp Bleaching, A Way to Reach High Brightness", Proceedings, 1990 TAPPI Pulping Conference, p. 265(1990).

7. STRUNK, W. G. and MENG, T., "Status Report: Pulp Bleaching With Hydrogen Peroxide During Refining", *Pulp and Paper* 60(11): 111(1986).

8a. KLEPPE, P. J., CHANG, H-M., and ECKERT, R. C., "Delignification of High Yield Pulp With Oxygen and Alkali: 1. Preliminary Studies on Southern Pine", *Pulp and Paper Mag. Can.* 73(12): 102(1972).

b. AKIM, G. L., "On the Degradation of Cellulose in Oxygen Bleaching", *Paperi Puu* 55(5): 389(1973).

9. LIEBERGOTT, N., VAN LIEROP, B., and BOLKER, H. I., "Comparing Different Alkalis in the Extraction Stages of Bleaching", *Trans. Tech. Sect. CPPA* 8(1): TR5 (1982).

10. HAFNER, V., HOEVELS, G., HOPF, B., KORN, W., NIMMERFROH, N., REINHOLD, A., SCHMIDT, K., and SUSS, H. U., "Sodium Carbonate as Alkali Source in Bleaching Mechanical Pulp", *Papier* 44(10): 521 (1990).

11. KATZ, S., LIEBERGOTT, N., and SCALLAN, A. M., "A Mechanism for the Alkali Strengthening of Mechanical Pulps", *TAPPI J.* 64(7): 97(1981).

12. MOLDENIUS, S., "Peroxide Bleaching Affects the Strength and Surface Properties of Mechanical Pulps", Proceedings, 1983 International Mechanical Pulping Conference, p. 51 (1983).

13. LEBO, S. E., LONSKY, W. F. W., McDONOUGH, T. J., MEDVECZ, P. J., and DIMMEL, D. R., "The Occurrence and Light-Induced Formation of *ortho*-Quinonoid Lignin Structures in White Spruce Refiner Mechanical Pulp", *J. Pulp and Paper Sci.* 16(5): J139(1990).

14. DAKIN, H. D., "Catechol", Organic Synthesis Collected Vol. 1., Gilman, H. ed., John Wiley & Sons, N.Y., p. 143 (1932).

15a. REEVES, R. H. and PEARL, I. A., "Reaction Products Formed Upon Alkaline Peroxide Oxidation Of Lignin-Related Model Compounds", *TAPPI J.* 48(2): 121(1965).

b. KEMPF, A. W. and DENCE, C. W., "The Reactions of Hardwood Lignin Model Compounds With Alkaline Hydrogen Peroxide", *TAPPI J.* 58(6): 104(1975).

c. GELLERSTEDT, G. and AGNEMO, R. "The Reactions of Lignin With Alkaline Hydrogen Peroxide. Part III. The Oxidation of Conju-gated Carbonyl Structures", *Acta Chemica Scandinavica* B34: 275(1980).

16a. GELLERSTEDT, G., HARDELL, H.-L., and LINDFORS, E.-L., "The Reactions of Lignin With Alkaline Hydrogen Peroxide. Part IV. Products From the Oxidation of Quinone Model Compounds", *Acta Chem. Scand.* B34: 669(1980).

b. PERO, R. W. and DENCE, C. W., "Methoxy-*p*-Benzoquinone and Methoxyhydroquinone As Models For Chromophore Changes in the Bleaching of Softwood Mechanical Pulps. II. The Effect of Peroxide Charge, Reaction pH, and Transition Metal Ions", *J. Wood Chem. and Tech.* 3(2): 195(1983).

17. HOCKING, M. B., *Can. J. Chem.* 51: 2384(1973).

18. HALL, R. E., "Peroxides and Peroxy Compounds, Inorganic", Kirk Othmer Encyclopedia of Chemical Technology. 3rd. ed. vol. 17, John Wiley & Sons, N.Y., pp. 10-11(1982).

19a. WAYMAN, M., ANDERSON, C. B., and RAPSON, W. H.,"Peracetic Acid Bleaching of Groundwood From Nine Canadian Wood Species", *TAPPI J.* 48(2): 113(1968).

b. McDONOUGH, T. J., "Effects of Chelating and De-Ashing Treatments on the Peracetic Acid Bleaching of Groundwood", *Pulp and Paper Magazine of Canada* 73(4): T79(1969).

20. SJÖGREN, G., DANIELSSON, J., ENGSTRAND, P., GELLERSTEDT, G., ZACHRISON, H., and REITBERGER, T., "The Importance of Radical Reactions for Brightness Increase in Hydrogen Peroxide Bleaching of Mechanical Pulps", Proceedings, 1989 Symposium on Wood and Pulping Chemistry, pp. 161-166(1989).

21. Toward the end of the experimentation, the batch size was reduced to 25 OD grams to extend the pulp supply. All reagent additions were adjusted accordingly.

22. Chemical Test Procedure 3 FMC Technical Bulletin 140, Hydrogen Peroxide for Chemical Pulp Bleaching(1984).

23. SKOOG, D. A. and WEST, D. M., Fundamentals of Analytical Chemistry. 2nd ed. New York: Holt, Rinehart and Winston, Inc., pp. 310-312(1969).

24. ANDTBACKA, A., HOLMBOM, B., and GRATZL, J. S.,"Factors Influencing the Light-Induced Yellowing and Bleaching of Spruce Groundwood", Proceedings, 1989 International Symposium of Wood and Pulping Chemistry, vol. 2, p. 347(1989).

Table IV. Results of 90-Minute Bleaching Experiments

EXP#	H_2O_2 %	NaOH %	Na_2CO_3 %	Brightness 90 min.	Residuals, % on Pulp			pH off
					H_2O_2	NaOH	$NaHCO_3$	
38.5	0	0	0	62.0	0	0	0	7
30.5	0	0	0	61.1	0	0	0	7
0.5	0	0	0	61.1	0	0	0	7
9.5	0	0	0	60.7	0	0	0	7
1	1.0	0.8	0	67.4	0.26	0.01	1.51	8.9
2	1.0	1.1	0	68.0	0.14	0.03	1.12	9.4
3	1.0	1.3	0	67.5	0.14	0.04	1.78	9.4
4	2.0	1.5	0	70.9	0.61	0.10	2.05	9.3
5	2.0	1.75	0	71.0	0.58	0.07	2.24	9.4
13	2.0	1.75	0	70.4	0.65	0.38	2.63	9.7
20	2.0	2.0	0	71.8	0.60	0.16	2.57	9.6
6	2.0	2.0	0	71.5	0.50	0.11	2.08	9.7
11	2.0	2.0	0	70.6	0.55	0.46	2.48	9.8
18	2.0	2.25	0	71.2	0.62	0.37	2.25	9.9
27	2.0	2.5	0	71.8	0.62	0.52	2.11	10.1
21	2.0	2.5	0	72.6	0.56	0.41	2.32	9.9
28	2.0	3.0	0	70.6	0.54	0.77	1.63	10.4
39	2.0	1.0	0.75	69.9	0.86	0.13	3.96	9.3
24	2.0	1.0	1.0	70.4	0.79	0.07	3.02	9.0
26	2.0	1.0	1.32	71.4	0.72	0.16	3.26	8.6
16	2.0	1.0	1.32	69.9	0.61	0.30	2.69	9.4
22	2.0	1.0	1.32	70.6	0.62	0.11	3.29	9.0
12	2.0	1.0	2.0	69.4	0.58	0.57	3.53	9.5
14	2.0	1.0	3.0	69.2	0.49	0.87	3.59	9.8
40	2.0	1.0	4.5	70.1	0.65	0.96	4.86	9.7
23	2.0	0.4	1.5	70.0	0.81	0.04	2.99	8.8
15	2.0	0.4	2.12	70.1	0.71	0.27	3.26	9.2
17	2.0	0.4	3.2	70.4	0.61	0.27	4.32	9.2
25	2.0	0.4	3.2	70.2	0.72	0.23	4.59	9.1
19	2.0	0.4	4.24	69.6	0.66	0.32	4.68	9.3
10	2.0	0.4	4.24	68.6	0.50	0.95	4.05	9.7
41	2.0	0.4	6.25	70.4	0.59	0.96	5.5	9.6
7	4.0	2.8	0	73.7	0.69	0.14	0.91	10.4
8	4.0	3.1	0	74.5	2.08	0.79	1.99	10.5
30	4.0	3.4	0	74.8	1.96	0.47	2.42	10.0
9	4.0	3.4	0	74.8	1.89	0.84	2.60	10.5
29	4.0	4.0	0	75.6	1.45	1.12	1.57	N.A.
31	4.0	4.6	0	77.2	1.71	1.65	0.66	10.9
32	4.0	5.2	0	72.8	N.A.	N.A.	N.A.	N.A.
43	4.0	2.3	1.3	74.8	N.A.	N.A.	N.A.	9.7
33	4.0	2.3	3.05	74.2	1.98	N.A.	N.A.	9.9
34	4.0	2.3	4.6	70.8	N.A.	N.A.	N.A.	N.A.
35	4.0	2.3	6.1	71.4	N.A.	N.A.	N.A.	N.A.
42	4.0	2.3	8.2	71.1	N.A.	N.A.	N.A.	N.A.
45	4.0	0.92	1.54	72.8	N.A.	N.A.	N.A.	8.8
36	4.0	0.92	4.88	74.2	N.A.	N.A.	N.A.	9.5
37	4.0	0.92	7.36	74.0	N.A.	N.A.	N.A.	9.6
38	4.0	0.92	9.75	71.3	N.A.	N.A.	N.A.	N.A.
44	4.0	0.92	12.8	73.4	N.A.	N.A.	N.A.	9.9

Table V. Peroxide Bleaching Data for 3-Hour Retention Times

EXP#	H2O2 %	NaOH %	Na2CO3 %	Brightness 3 Hours	Residuals, % on Pulp			pH off
					H_2O_2	NaOH	$NaHCO_3$	
0	0	0	0	61.1	0	0	0	7
9.5	0	0	0	60.7	0	0	0	7
30.5	0	0	0	61.1	0	0	0	7
38.5	0	0	0	62.0	0	0	0	7
30	4.0	3.4	0	76.9	2.00	0.46	2.9	9.8
29	4.0	4.0	0	77.5	1.45	1.12	1.57	10.5
31	4.0	4.6	0	77.8	1.37	1.57	1.27	10.9
32	4.0	5.2	0	75.4	1.17	1.55	0.69	11.1
43	4.0	2.3	1.3	76.1	1.85	0.5	3.77	9.5
33	4.0	2.3	3.05	75.2	1.66	0.88	4.1	9.6
34	4.0	2.3	4.6	72.6	1.54	1.39	4.56	9.8
35	4.0	2.3	6.1	73.9	1.43	1.83	5.04	9.8
42	4.0	2.3	8.2	73.2	0.78	4.04	2.2	10.9
45	4.0	0.92	1.54	74.6	2.09	0.11	3.29	9.0
36	4.0	0.92	4.88	74.7	1.62	0.54	5.97	9.3
37	4.0	0.92	7.36	74.1	1.22	1.18	6.76	9.5
38	4.0	0.92	9.75	73.3	1.01	1.89	7.13	9.7
44	4.0	0.92	12.8	74.9	1.07	2.83	8.18	9.6