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D.J. Senior, J. Hamilton, A.J. Ragauskas, P. Froass, and J. Sealey

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INTERACTION OF HYDROGEN PEROXIDE AND CHLORINE DIOXIDE STAGES IN ECF BLEACHING

D.J. Senior

ICI Forest Products, 2101 Hadwen Road, Mississauga,
Ontario, L5K 2L3, Canada

J. Hamilton

A.J. Ragauskas

J. Sealey

Institute of Paper Science and Technology
500 100th Street N.W., Atlanta, GA, 30318
U.S.A.

P. Froass

ABSTRACT

The order of hydrogen peroxide (P) and chlorine dioxide (D_1) stages in an ECF sequence has been shown to affect the final brightness in Southern and Northern softwood and eucalypt kraft pulps. The Southern softwood pulp bleached using the sequence DEopDPP had consistently higher interstage and final brightnesses than the DEopPDP sequence. Northern softwood and eucalypt pulps were each bleached using DEDP and DEPD sequences. In each case higher brightnesses were achieved when the D_1 stage preceded the P stage. The effect was especially evident with the hardwood pulp where over 3% ISO points higher brightness was seen for the DEDP sequence. Lignin was extracted from the brownstock, DE-stage, DEP stage and DED stage pulps and analyzed by ^{31}P NMR. The aromatic lignin content of softwood pulp was reduced by 60% following the D_1 stage (DED) but was essentially unchanged when treated by peroxide (DEP). For the hardwood pulp, lignin content following the D_1 stage (DED) was reduced by 90-95%. The improved bleaching response of the DEDP pulp in comparison to the DEPD pulp is consistent with documented reactivities of hydrogen peroxide and chlorine dioxide toward specific lignin structures. In the DEDP sequence, chlorine dioxide of the D_1 stage reduces the aromatic content of pulp so that the following hydrogen peroxide stage can more effectively react with non-aromatic species. Conversely, during bleaching with a DEPD sequence, the P-stage is less effective in reducing aromatic lignin content prior to the D_1 stage and therefore is beneficial to a lesser degree prior to the D_1 stage. This effect is clearly manifested as a lower brightness. It is also reflected as a reduced sensitivity to bleaching with increasing hydrogen peroxide charges.

INTRODUCTION

Hydrogen peroxide has been in routine use in the bleaching of mechanical pulps for many years (1) and is now of greater importance in kraft mills as an addition to extraction stages or as full P stages. Increasing the use of hydrogen peroxide in ECF bleaching has allowed a reduction in chlorine dioxide use in both shortened (2,3) and full bleach sequences (2,4,5). These

reductions may overcome generator capacity limitations or may be part of a program to optimize overall bleaching costs (4,6,7). Hydrogen peroxide may also be in use to lower chlorine dioxide demand and reduce AOX in ECF bleaching. Full-scale mill studies already indicate that extensive environmental gains can be realized by the move to ECF bleaching (8,9).

Earlier work by Gellerstedt and Pettersson (10) identified optimal conditions for use of hydrogen peroxide. This includes strict control of transition metal concentration in pulps (11) and stabilizing hydrogen peroxide from decomposition to cellulose-damaging free radical formation (5,11-15). Another prerequisite in hydrogen peroxide bleaching to high brightness is that the pulps be as fully delignified as possible prior to entering the bleach plant (3, 16-18). Thus, extended cooking and oxygen delignification will play an important role in optimizing hydrogen peroxide use. The best conditions for hydrogen peroxide bleaching should typically employ high consistency, high temperatures, and long residence times (3,5,10,17,19,20). Optimization of caustic, hydrogen peroxide, magnesium, and silicate levels is also necessary (10,20). There has been considerable interest in the additional brightness gains that can be realized by employing high temperature pressurized peroxide stages (18,19,21-23). However, this application has only had a limited impact at the mill scale in ECF bleaching (22).

Recently, van Lierop, Liebergott and Faubert (2) demonstrated how a hydrogen peroxide reinforced extraction stage could affect chemical consumption, brightness and AOX when applied in various positions of the bleach sequence. Devenyns *et al.* evaluated the potential of hydrogen peroxide to replace chlorine dioxide when applied either as a prebleaching or final brightening stage (5). Similarly, the impact of the position within the bleach sequence of a hydrogen peroxide (pressurized) stage on equipment layout and chemical consumption efficiency has been discussed (7). There exists a tremendous volume of hydrogen peroxide bleaching data in the literature and the studies such as those above reflect efforts to optimize its use. Despite these facts there is very little information that considers the impact that a hydrogen peroxide stage may have on the performance of a subsequent chlorine dioxide stage or *vice versa*.

An extensive evaluation by Malinen, Rasimus and Rantanen (6) focussed on minimizing the use of chlorine dioxide in bleaching of pulps to high brightness. Closer re-examination of the bleaching data of the 36 different ECF sequences that were used reveals a unique common feature; brightnesses were consistently higher when a chlorine dioxide (D_1) stage preceded an alkaline hydrogen peroxide-reinforced extraction stage. Similarly, the final D_2 brightness of pulps produced in this manner were higher.

An ECF bleaching evaluation was conducted in our laboratory on a Southern softwood pulp using the sequence DEopPDP. When the sequence order was reversed (DEopDPP), an increase in brightness was consistently observed. These results were

consistent with the Malinen et al. study and suggested that the order of chlorine dioxide and hydrogen peroxide as D₁ and P stages might influence each other by either chemical or physico-chemical means. When this work was repeated on other hardwood and softwood pulps the same effect was seen.

In this paper, data are presented which demonstrate that the order of chlorine dioxide and hydrogen peroxide addition impact the performance of each other. The phenomenon is discussed with regard to the reactivity of chlorine dioxide and hydrogen peroxide to the changing structure of lignin during bleaching.

EXPERIMENTAL

Bleaching experiments were carried out on brownstock softwood and hardwood pulps. Two softwood pulp samples were studied; the first sample was a Southern U.S. softwood with a Kappa number of 28.0 and the second was an Eastern Canadian softwood, Kappa number 26.6. The hardwood sample was a South American eucalypt, Kappa number 12.4.

Large 300g batches were prepared for lignin extraction and analysis; smaller (30 or 20g) samples were employed for the bleaching runs. Chemical charges are expressed as percent on oven-dried unbleached pulp.

All pulp samples were washed at 1% consistency and filtered to 25-30% consistency between stages. Acid washing was achieved by adding dilute sulphuric acid to a pH of 2 in the 1% consistency wash.

Chlorine Dioxide (D)

Chlorine-free chlorine dioxide was prepared by determining the exact amount of chlorine present in the solution and adding the stoichiometric equivalent of sodium chlorite.

D₁₀₀ stages were carried out at 3.5% consistency and 50°C for 30 minutes. Kappa factors of 0.15, 0.18 and 0.20 were applied to the Southern U.S. sample; the Eastern Canadian and eucalypt pulps employed Kappa Factors of 0.18, and 0.10, respectively. Acidification was necessary to achieve optimum first stage delignification in the hardwood.

D₁ stages utilized the following conditions: consistency, 6%; temperature, 80°C; retention time, 180 minutes. Typically, caustic soda was also added to maintain an exit pH of 3.5-4.3. A dose of 1.2% was applied to the Eastern Canadian and hardwood pulps; two charges of 0.6 and 1.0% were employed in the Southern U.S. pulp study.

Chlorine dioxide stages were carried out in glass Mason jars; it was necessary to combine several smaller runs to achieve the large samples required for lignin analysis.

Caustic Extractions (E)

Extractions were performed on 150 or 20g lots (as required) by adding caustic soda and the required amount of water to the pulp and stirring in a Hobart mixer. The pulp was then transferred to a polyethylene bag and placed in a constant temperature bath at 80°C for 60 minutes. For the Southern U.S. sample only, the extraction stage was applied at 2.8% and fortified with oxygen and 0.4% hydrogen peroxide. The Eastern Canadian and hardwood samples utilized caustic charges of 2.5 and 2.2%, respectively.

Hydrogen Peroxide

Charges of 1.0 and 0.5% were applied in the two P stages, respectively, of the Southern U.S. softwood. A peroxide dose of 2.0% was applied for both the Eastern Canadian and hardwood samples. Sodium hydroxide was added as necessary to achieve optimum pH of around 11. Conditions were as follows: consistency, 12%; temperature, 80°C; retention time, 120 minutes. Magnesium sulfate was included at 0.05% (on pulp) as part of the bleach liquor which was mixed with the pulp samples in a Hobart mixer. The pulp slurry was then transferred in a polyethylene bag to a constant temperature bath.

Chemical residuals were determined by iodometric titration and expressed as percent oven dry weight of pulp. Brightnesses are reported as % ISO brightness and measured using a Zeiss Elrepho photoelectric reflectance photometer on 4g (o.d.) sheets.

Residual Lignin Isolation Procedure

Residual lignins were isolated by mild acid hydrolysis as described by Gellerstedt (24). Slight modifications to Gellerstedt's procedure were made with the complete procedure as follows: the bleached and unbleached pulps were acetone extracted and air dried. The pulps were then washed with distilled water and air dried. Residual lignin extraction was performed with a 9:1 dioxane to water ratio with a 0.1 HCl solution at a 4% consistency. The extraction was refluxed for two hours. The solution was filtered, and the filtrate was passed through celite. The solution was then neutralized to pH 7 and concentrated. During concentration distilled water was added. After all the dioxane was removed, the solution was precipitated by acidifying to pH 2.5. The residual lignins were centrifuged, and washed with distilled water three times and then freeze-dried. The average yield was 40% (based on Kappa numbers).

³¹P - NMR Analysis of Residual Lignin

Residual lignin characterization was performed by ³¹P NMR analysis described by Argyropoulos (25). 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was used as the phosphorylation reagent in this quantitative analysis. Two stock solutions were prepared. The first was a solution of pyridine and

deuterated chloroform in a 1.6/1 v/v ratio, which was used as the solvent for the residual lignins. The second solution was chromium(III) acetylacetonate in cyclohexanol (5.0 mg/ml). The chromium(III) acetylacetonate was used as the relaxation reagent, and the cyclohexanol was used as the internal standard. The ^{31}P NMR samples were prepared by adding 400 μl of the solvent solution and 150 μl of the relaxation reagent solution to 25 mg of residual lignin. This solution was stirred while 45 μl of phosphitylation reagent was added, and this solution was allowed to stir for two minutes before being transferred into an NMR tube and tested. NMR analysis was performed on a Bruker 400 DMX with a 25-second delay and 200 scans. All chemical shifts are relative to the reaction product of water with the phosphitylation reagent which gives a sharp signal at 132.2 ppm.

RESULTS AND DISCUSSION

During the course of ECF bleaching of a softwood kraft pulp from a Southern U.S. mill, an observation was made that the order of hydrogen peroxide (P) and chlorine dioxide (D_1) stages consistently affected the brightness of the pulps. Specifically, when the D_1 stage was placed before the P stage, the brightness of the pulp was higher. The work was extended to another softwood and hardwood pulp to confirm the observation. Some simple kinetic studies were initiated as well as extracting various lignin samples for structural analysis as a means to identify if the effect was physical and/or physico-chemical in nature.

The initial objective of the bleaching study using the Southern softwood pulp was to identify the final brightnesses obtained using several different ECF sequences. This particular mill is converting from use of chlorine and hypochlorite in its bleach sequence to an ECF sequence and was interested in the potential of using the redundant hypochlorite tower as a hydrogen peroxide (P) stage tower. The chemical charges and bleaching conditions were supplied by the mill which produced the pulp. In Table 1a, various interstage and final brightnesses are shown for the sequence DEopPDP. Using this sequence, the highest Kappa Factor applied in the D_{100} stage resulted in a final brightness of 87.8% ISO. When the same pulp was pretreated with xylanase (Ecopulp® X-200), an additional point in brightness was reached (89.2% ISO) which indicated that a further gain in brightness could be possible. A similar gain was also seen at each of the lower Kappa Factors used with or without enzyme. The additional brightness gains seen when using the enzyme pretreatment suggested that the pulp had hit a brightness ceiling with the DEopPDP sequence. When the bleaching was repeated with switching the P_1 and D_1 stages to a DEopDPP sequence, the final brightnesses also increased by a point, again at each Kappa Factor applied (Table 1b).

A comparison of the brightnesses for the DEopDPP and DEopPDP sequences before the second P stage (DEopDP and DEopPD brightnesses compared, respectively) shows an even more obvious brightness difference at each Kappa Factor. Residual peroxide after the P stage was about 10% of the applied charge for either

sequence. Peroxide stages were conducted to maintain the extraction stage at about pH 10. Thus, for this pulp, the final brightness was clearly higher when the D_1 stage preceded the P_1 stage.

This comparison was then applied to a Northern softwood pulp to see if the order of D_1 and P_1 stages had a similar effect. The sequences were simplified to DEPD and DEDP to eliminate the effects of oxygen and hydrogen peroxide reinforcement in the extraction stage which could interfere with the comparison. Using identical chemical charges and conditions, the DEDP sequence produced a pulp with about 1 brightness point higher than the DEPD sequence (Table 2a). Similarly, a comparison of brightnesses using a hardwood (eucalypt) kraft pulp with the same sequences was made. In this case the difference in brightness using the DEDP sequence was a full 3% ISO higher than the DEPD sequence (Table 2b). Clearly, the placement of the D_1 before the P_1 stage permitted higher brightnesses to be reached, using both hardwood and softwood pulps.

It was immediately assumed that the higher final brightness of the DEDP pulp over the DEPD pulp could be attributed to the improved P-stage performance because of the removal of metals. Presumably this would be a result of the acidic wash effect of the D_1 stage. An economic way of performing a mild acid wash to reduce transition metals is to employ a chlorine dioxide stage prior to the P stage (2,5) or acidic filtrate wash (20).

To determine if the levels of metals might play a role in the performance of the P stage, metal levels were measured for the Northern softwood and hardwood pulps in the brownstock, post DE-stage, and after a dedicated acid wash (DEA) (Table 3). The manganese level of the softwood brownstock was quite high (114 ppm) but was lowered to 10 ppm by the acidic effect of the first D stage. An additional acid wash reduced the manganese level to below 4 ppm. The hardwood brownstock pulp had a much lower manganese level; the DE treatment and acid stage dropped the level to < 2 and 0.5 ppm, respectively. Iron content of either pulp was only slightly affected by acidic treatments.

The improved performance of the peroxide stage, following the acid wash (DEAPD) sequence can be seen by comparing the P-stage brightnesses (Table 2a). Reducing the manganese level from 10 to 4 ppm permitted a brightness gain of over 1.5% ISO points. However, this gain was not passed to the post- D_1 brightness to any significant extent. Conversely, the acid wash placed before the D_1 stage (DEPAD) gave a slight increase in brightness.

The kinetics of chlorine dioxide consumption by pulps and formation of associated species has been documented (26-30). Typically a bi-phasic reaction characterizes a very rapid conversion of chlorine dioxide involving free radicals, followed by bleaching at a much slower rate with various radical and ionic species (30). Concomitant with the generation of these species is a drop in pH because of their largely acidic nature.

As a general measure of the kinetic profile of the D_1 stages, the development of acidic species with its associated drop in pH during this stage was measured. The drop in D_1 -stage pH is shown for the bleaching of the hardwood pulps in Figures 1a-d. Starting with an initial pH of 9.5 and a final pH of 3.5, the DEDP sequence developed the highest brightness (87.6% ISO) (Figure 1a). The sequence DEPD had a final brightness 3% ISO points lower but also had a slightly higher exit pH (Figure 1b) which could be expected to reduce brightness development (31,32). Thus, an acid wash was done to remove metals prior to the P stage (DEAPD) (Figure 1c) or the D_1 stage (DEPAD) (Figure 1d). In both cases the exit pH's would be expected to yield a comparable brightness as the DEDP stage since the D stage exit pH's were all similar. However, in each case where the P stage preceded the D_1 stage, the final brightness was lower. In the case of the softwood pulps (Figures 2a-c) the differences in brightness for the various sequences are too small to discuss with respect to exit pHs. It is also interesting to note that, in each case (hardwood or softwood), when the P stage preceded the D_1 stage, the pH/time curves for the D_1 stage appears to be triphasic. This may imply the development of different intermediate bleaching species from the DEDP sequence, which could account for the differences in final brightnesses. This will be investigated later.

One explanation for the difference in final brightness of the DEDP and DEPD pulps is that the order of addition of the D_1 and P stages, (DP vs PD) might affect the reactivity of the lignin in the pulp to the subsequent stage. In the case of the DEDP sequence, the D_1 stage may create a lignin that is very susceptible to reaction with the following P stage, thus resulting in the high final brightness. Conversely, in the case of the DEPD sequence, the P stage may leave the lignin in a manner that the D_1 stage cannot raise the brightness to the same extent as the DEDP sequence.

To determine if there could be a chemical basis for the difference in bleaching response of DEDP and DEPD pulps, an analysis of the lignins during the bleach sequences was done by ^{31}P NMR. This technique has recently been applied by Sun and Argyropoulos to understand the mechanism of oxygen or Eop delignification by studying the changes in lignin structure during each process (33).

Lignin was extracted from unbleached, DE, DEP and DED stages of both softwood and hardwood pulps and prepared for ^{31}P NMR analysis. The most notable differences are in the phenolic and condensed lignins contents of softwood (Figure 3) and hardwood (Figure 4) pulps.

In the hydrogen peroxide-treated softwood pulp (DEP), the phenolic and lignin contents are virtually identical to the DE pulp (Figure 3a,b). However, both species are reduced by about 60-70% after the D_1 stage (DED pulp). Thus, in the case of the DEPD sequence, the D_1 stage must act on DEP pulp that has a phenolic lignin content identical to the DE stage; the P stage of the DEP pulp has done nothing to lower the phenolic content prior to the D_1 stage. It is known that, under the practical conditions of bleaching,

chlorine dioxide reacts mainly with phenolic hydroxyl lignin (34). Therefore in the case of the DEPD pulp, the hydrogen peroxide stage has done very little to remove the target substrate of the D_1 stage and a lower brightness results. Conversely, the phenolic contents of DED pulps are removed by 60-70%. The products of chlorine dioxide treatments include various quinones and other conjugated chromophores (34-39). Although some of these are removed by various degradation products of chlorine dioxide, such as chlorine, chlorous acid, hypochlorous acid, many of the products of the D_1 stage are known to be sensitive to alkaline hydrogen peroxide treatment. It is known that alkaline hydrogen peroxide, when used as it is here, is an anionic bleaching agent that brightens by acting on carbonyl and conjugated carbonyl structures, including quinones (35), rather than aromatic structures. Therefore, for the DEDP sequence, the D_1 stage acts to bleach and remove lignin and in doing so, it prepares the pulp for subsequent treatment by hydrogen peroxide. Therefore it is not unexpected that the DEDP pulp is brighter than the DEPD pulp. [Note that free radical (HO_2^\bullet) formation does occur with hydrogen peroxide which can attack the aromatic groups in lignin (40), but reaction conditions (pH, metal levels, magnesium-to-manganese ratio) are optimized to minimize this formation of free radicals which attack both lignin and cellulose indiscriminately thus leading to strength loss].

The difference in brightness of the DEPD and DEDP pulps was even greater in the hardwood case than the softwoods. Analysis of the hardwood lignin by ^{31}P NMR supports this difference. Similar to the softwood pulp, treatment of DE hardwood pulp with chlorine dioxide (D_1) resulted in a significant reduction in lignin content. Both condensed lignins concentration (Figure 4a) and phenolic content (for the hardwood case, resolution of phenolics content to guaiacyl and demethylated phenolic (Figure 4b) and syringyl phenolics content (Figure 4c) was possible) were reduced by 90-95% as compared to about 60-70% for the softwood pulp. Unlike the softwoods, however, treatment of the hardwood DE pulp with hydrogen peroxide resulted in removal of greater than 50% of the phenolics and lignins content. Another difference between hardwood- and softwood-treated pulps was that the aliphatic hydroxyl content of pulp following hydrogen peroxide treatment of DE pulp was reduced whereas this content was increased following chlorine dioxide treatment (Figure 4d). Essentially, no change was seen in the softwood experiments. Another difference with the hardwoods was that the carboxylic acid concentration of the DED pulp was almost 50% lower than either the DE or DEP pulps (Figure 4e). The softwood pulp showed very little difference.

The review of the mechanisms of pulp bleaching above by hydrogen peroxide and chlorine dioxide reveals that each agent is most effective acting on specific structures. Specifically, chlorine dioxide strongly attacks aromatic species; whereas, hydrogen peroxide preferentially attacks carbonylic and conjugated carbonylic species. Pulps are more susceptible to treatments with hydrogen peroxide when the lignin content is reduced by prior treatment with chlorine dioxide. The lignin by-products of chlorine

dioxide treatment may also be more susceptible to hydrogen peroxide treatment. The net effect is that for the DEDP pulp (hardwood or softwood), the D₁ stage functions to remove lignin and allows the subsequent P stage to be more effective. Conversely, for the DEPD softwood sequence, the P stage appears to be totally ineffective in reacting with lignin of the DE pulp. This leaves the D₁ stage to have to act on pulp that is essentially identical to the DE pulp. Thus a reduced brightness would be expected. For the hardwood case, a similar argument can be made; however, hydrogen peroxide treatment of DE pulp was useful in lowering lignin content of DE pulp, but not nearly as much as chlorine dioxide treatment. In every case a higher brightness would be expected where a D₁ stage precedes the P stage.

This hypothesis is also supported by monitoring the final brightnesses of pulps when treated over a range of P-stage charges. The final brightnesses of softwood DEDP and DEPD pulps when treated over a range of hydrogen peroxide charges is shown in Figure 5. As above, the final DEPD brightnesses are lower than the DEDP sequence. In addition, as the P-stage charge of the DEPD sequence increases, the brightness development of the pulp is less than the DEDP sequence, as indicated by the flatter curve. This indicates, perhaps, a limitation of the concentrations of hydrogen peroxide-sensitive groups in the pulps. The brightness limitation and insensitivity to increasing hydrogen peroxide charge for the DEPD sequence may be due to less available or less reactive substrate for the hydrogen peroxide. This is supported by the structural evidence presented above.

CONCLUSIONS

Various kraft pulps were bleached using ECF sequences containing a peroxide stage. Brightnesses were consistently higher when the D₁ stage preceded the P stage(s). Analysis of the lignin extracted during the course of bleaching provides an explanation in support of this observation. In the case of DEDP sequences, the D₁ stage effectively removes lignin from the pulp thereby facilitating the P stage reactions and allowing high brightness to be reached. Conversely, the hydrogen peroxide stage of the DEPD sequence is ineffective at lignin removal in softwoods and removed about 60-70% of lignin in hardwoods. For both cases, however, the P stage is less effective for lignin removal than the D₁ stage and therefore final brightnesses are lower.

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REFERENCES

1. Andrews, D.H., and Singh, R.P. *The Bleaching of Pulp*, 3rd Edition "Peroxide Bleaching" Tappi Press, Atlanta, Ed. by R. Singh, Chp. 8: 211-253 (1979).
2. van Lierop, B., Liebergott, N., and Faubert, M. *Preprints, 1993 Spring Conference, CPPA*, "Inclusion of a mild D-stage in EopQP and OQP Sequences" 1-8 (1993).
3. Parthasarathy, V.R., Rudie, G.F., Detty, A.E., Farley, B.R., French, N.H., and Chandrasekaran, S. *Preprints, 1993 Pulping Conference*, "Total chlorine dioxide substitution in short sequence bleaching and its effect on pulp brightness and effluent characteristics" 933-949 (1993).
4. Lachapelle, R.C., Strunk, W.G., and Klein, R.J. *Tappi Journal*, "Using hydrogen peroxide in 100% chlorine dioxide bleaching sequences" 75(7): 181-186 (1992).
5. Devenyns, J., Renders, A., Carlier, J., and Walsh, P. *Preprints, 1995 Pulping Conference*, "Optimal use of hydrogen peroxide to design low AOX ECF sequences" 281-288 (1995).
6. Malinen, R., Rasimus, R. and Rantanen, T. *Preprints, 1993 Pulping Conference*, "ECF bleaching of oxygen-delignified softwood pulp with minimum charge of ClO₂" 925-931 (1993).
7. Reeves, R., Boman, R., and Nordén, S., *Preprints, 1995 Pulping Conference*, "Impact of sequence position for pressurized (PO) stage in ECF bleaching," 263-279 (1995).
8. Pryke, D.C., Swanson, S.M., Kloepper-Sams, P.J., Bouree, G.R., and Owens, J.W. *Pulp and Paper Canada*, "Environmental Improvements at Grande Prairie and Ecosystem Response" 95(6): T230-236 (1994).
9. Pryke, D.C., Bouree, G.R., Winter, P., and Mickowski, C. *Pulp and Paper Canada*, "The impact of chlorine dioxide delignification on pulp manufacture and effluent characteristics at Grande Prairie, Alberta" 96(11): 41-49 (1995).
10. Gellerstedt, G. and Pettersson, I. *J. Wood Chemical and Technology*, "Chemical aspects of hydrogen peroxide bleaching. Part II * The bleaching of kraft pulps" 2 (3): 231-250 (1982).
11. Lapiere, L., Bouchard, J., Berry, R.M., and van Lierop, B. *J. Pulp and Paper Science*, "Chelation prior to hydrogen peroxide bleaching of kraft pulps: An overview" 21 (8): J268-J273 (1995).
12. Basta, J., Holtinger, L., Hermansson, W., and Lundgren, P. *Preprints, 1994 International Pulp Bleach Conference, Papers*, "Metal Management in TCF/ECF Bleaching. Part I - TCF Bleaching", 29-32 (1994).
13. Troughton, N., and Sarot, P., *Preprints, 1992 Pulping Conference* "The efficient use of hydrogen peroxide as a chemical pulp delignification agent: The Macroxsm Process", 519-529 (1992).

14. Bouchard, J., Nugent, H.M., and Berry, R.M. *J. Pulp and Paper Science*, "A comparison between acid treatment and chelation prior to hydrogen peroxide bleaching of kraft pulps" 21 (6): J203-J208 (1995).
15. Devenyns, J., Desprez, F., and Troughton, N.A. *Preprints, 1993 Pulping Conference* "Peroxygen prebleaching and bleaching technologies for step-wise conversion from conventional chlorine bleaching via ECF to TCF" 341-352 (1993).
16. Troughton, N.A., Desprez, F., and Devenyns, J. *Preprints, 1994 Pulping Conference*, "P₁₀₀ TCF bleaching of softwood kraft pulps to high brightness" 807-820 (1994).
17. Desprez, F., Devenyns, J., and Troughton, N. *Preprints, 1993 Pulping Conference*, "P": One-stage hydrogen peroxide full bleaching of previously delignified softwood kraft pulp" 443-452 (1993).
18. Germgård, U. and Nordén, S. *Preprints, 1994 International Pulp Bleaching Conference Papers*, "OZP - Bleaching of kraft pulps to full brightness" 53-58 (1994).
19. Desprez, F., Devenyns, J., and Troughton, N.A. *Preprints, 1994 Pulping Conference*, "TCF bleaching of softwood kraft pulp: The optimal conditions for P* hydrogen peroxide bleaching" 929-934 (1994).
20. van Lierop, B., Liebergott, N., and Faubert, M.G., *Preprints, 79th Ann. Meet. Tech. Section, CPPA* "Using oxygen and peroxide to bleach kraft pulps", B81-B99 (1993).
21. Devenyns, J., Desprez, F., and Troughton, N. *Preprints, 1994 International Pulp Bleaching Conference, Posters*, "The hydrogen peroxide P* approach to TCF final brightening" 57-60 (1994).
22. Boman, R., Reeves, R. and Nordgren, B., *Pulp and Paper* "Mills improve bleach results with pressurized peroxide (PO)," October: 121-125 (1995).
23. Stromberg, B., and Szopinski, R., *Preprints, 1994 International Pulp Bleaching Conference*, "Pressurized hydrogen peroxide bleaching for improved TCF bleaching" 199-209 (1994).
24. Gellerstedt, G. and Lindfors, E., *Preprints, 1991 International Pulp Bleaching Conference* "On the structure and reactivity of residual lignins in kraft pulp fibers" 73-88 (1991).
25. Granata, A., and Argyropoulos, D. *J. Agric. Food Chem.* "2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins" 43: 1538-1544 (1995).
26. Wartiovaara, I. *Preprints, 1985 International Pulp Bleaching Conference* "Reaction mechanism of effective chlorine dioxide bleaching" 7-11 (1985).
27. Reeve, D.W., and Weishar, M. *Tappi Journal* "Chlorine dioxide delignification - process variables" June:164-167 (1991).
28. Ni, Y., and van Heiningen, A.R.P. *Nordic Pulp and Paper Res. J.*, "Mechanism of formation of chloro-organics during chlorine dioxide prebleaching of kraft pulp" 8 (4):350-351, 378 (1993).
29. Ni, Y., Kubes, G.J. and van Heiningen, A.R.P. *Nordic Pulp and Paper Res. J.* "Rate processes of AOX formation and chlorine species distribution during ClO₂ prebleaching of kraft pulp" 7 (4):200-205 (1992).
30. Brage, C., Eriksson, T., and Gierer, J. *Holzforschung* "Reactions of chlorine dioxide with lignins in unbleached pulps" 45 (1):23-30 (1991).
31. Wartiovaara, I., *Paperi Ja Puu* "The influence of pH on the D stages DE and ODE bleaching sequences" 10: 581-584 (1982).
32. Basta, J., Andersson, L., Blom, C., Holtinger, L., and Hook, J., *Appita Journal* "Reducing AOX levels Part 2: Chlorine-free bleaching" 217-221 (1991).
33. Sun, Y., and Argyropoulos, D.S. *J. Pulp and Paper Science* "Fundamentals of high-pressure oxygen and low-pressure oxygen (Eop) delignification of softwood and hardwood kraft pulps: A comparison" 21(6): J185-J190 (1995).
34. Ni, Y., Kubes, G.J., and van Heiningen, A.R.P. *Preprints, 1993 Spring Conference, CPPA* "Fundamentals of delignification during D₁₀₀ bleaching" 1-8 (1993).
35. Gierer, J. *Holzforschung* "Basic principles of bleaching" 44(6): 395-400 (1990).
36. Ni, Y., Shen, X. and van Heiningen, A.R.P. *J. Wood Chem. Tech.* "Studies on the reactions of phenolic and non-phenolic lignin model compounds with chlorine dioxide" 14(2): 243-262 (1994).
37. McKague, A.B., Reeve, D.W., and Xi, F. *Nordic Pulp and Paper Res. J.* "Reaction of lignin model compounds sequentially with chlorine dioxide and sodium hydroxide (2): 114-118 (1995).
38. Dence, C.W., Gupta, M.K., and Sarkanen, K.V. *Tappi Journal* "Studies on oxidative delignification mechanisms Part II. Reactions of vanillyl alcohol with chlorine dioxide and sodium chlorite" 45(1): 29-38 (1962).
39. Gellerstedt, G., and Agnemo, R., *Acta Chemica Scandinavica* "The reactions of lignin with alkaline hydrogen peroxide. Part III* The oxidation of conjugated carbonyl structures" B34: 275-280 (1980).
40. Gierer, J., Jansbo, K., and Reitberger, T. *J. Wood Chem. Tech.* "Formation of hydroxyl radicals from hydrogen peroxide and their effect on bleaching of mechanical pulps" 13(4): 561-581 (1993).

TABLE 1a
ECF SEQUENCE, DE_{op}PDP BLEACHING OF SOUTHERN SOFTWOOD KRAFT PULP

CONTROL PULPS												
D ₁₀₀			E = 2.8% P = 0.4%	1.0% H ₂ O ₂ 0.05% MgSO ₄ , 0.45% NaOH			0.6, 1.0% ClO ₂ 0.1% NaOH			0.5% H ₂ O ₂ 0.35% NaOH		
D ₁₀₀ ClO ₂ Charge (% on pulp)	D ₁₀₀ Exit pH	D ₁₀₀ Residual (% on pulp)	E _{op} Brightness (% ISO)	pH	Residual (% on pulp)	P - Stage Brightness (% ISO)	Exit pH	Residual (% on pulp)	D ₁ - Stage Brightness (% ISO)	pH	Residual (% on pulp)	Final Brightness (% ISO)
1.59 [0.15 KF]	2.4	-	50.0	10.7/10.3	0.14	60.6	3.7	-	78.0	10.6/9.6	0.03	81.6
							3.8	-	82.7	10.8/9.3	0.02	85.3
1.91 [0.18 KF]	2.3	0.03	54.4	10.6/9.6	0.12	65.8	3.8	0.02	83.6	10.7/9.4	-	85.6
							3.2	0.03	86.0	10.7/9.1	0.035	87.8
2.12 [0.20 KF]	2.3	0.04	54.1	10.6/10.1	0.14	67.8	3.7	0.03	82.7	10.5/9.3	0.12	85.8
							3.3	0.05	86.7	10.8/9.2	0.03	87.8
XYLANASE - TREATED PULPS												
1.56 [0.15 KF]	2.4	-	51.0	10.6/10.2	0.22	61.7	3.6	-	79.2	10.8/9.7	0.02	82.7
							3.2	0.01	83.6	10.8/9.4	0.025	86.5
1.88 [0.18 KF]	2.4	0.05	55.5	10.7/9.8	0.12	67.1	3.8	0.06	84.1	10.8/9.7	-	86.4
							3.3	0.08	86.6	11.0/9.3	0.035	88.9
2.08 [0.20 KF]	2.3	0.06	55.7	10.7/10.4	0.17	68.3	3.7	0.13	83.5	10.7/9.6	0.11	86.4
							3.3	0.15	86.9	10.9/9.4	0.03	89.2

[KF] = Kappa factor
E = Caustic soda extraction
P = Hydrogen peroxide

TABLE 1b
ECF SEQUENCE, DE_{op}DPP BLEACHING OF SOUTHERN SOFTWOOD KRAFT PULP

CONTROL PULPS													
D ₁₀₀			E = 2.8% P = 0.4%	0.6, 1.0% ClO ₂ 0.1, 0.2% NaOH				1.0% H ₂ O ₂ 0.05% MgSO ₄ , 0.45% NaOH			0.5% H ₂ O ₂ 0.35% NaOH		
D ₁₀₀ ClO ₂ Charge (% on pulp)	D ₁₀₀ Exit pH	D ₁₀₀ Residual (% on pulp)	E _{op} Brightness (% ISO)	D ₁ Charge (% on pulp)	Exit pH	Residual (% on pulp)	D ₂ - Stage Brightness (% ISO)	pH In/out	Residual (% on pulp)	P - Stage Brightness (% ISO)	pH	Residual (% on pulp)	Final Brightness (% ISO)
1.59 [0.15KF]	2.4	-	50.0	0.6	3.7	-	73.5	10.5/9.4	0.07	82.4	10.7/10.2	0.01	82.8
				1.0	3.7	-	77.6	10.4/9.5	0.08	85.9	10.8/10.3	0.01	85.6
1.91 [0.18 KF]	2.3	0.03	54.4	0.6	4.0	0.04	78.8	10.4/10.0	0.04	85.1	10.8/10.2	0.02	85.2
				1.0	3.4	0.12	82.0	10.4/10.1	0.12	87.2	10.8/10.2	0.03	87.5
2.12 [0.20 KF]	2.3	0.04	54.1	0.6	3.5	0.02	79.3	10.5/9.7	0.11	86.1	10.7/10.0	0.03	86.8
				1.0	3.4	0.18	82.4	10.5/9.6	0.18	87.3	10.7/10.1	0.02	88.5
XYLANASE - TREATED PULPS													
1.56 [0.15 KF]	2.4	-	51.0	0.6	3.6	0.01	73.8	10.5/9.8	0.18	83.2	10.8/10.3	0.01	83.7
				1.0	3.6	0.06	79.0	10.5/9.9	0.27	87.4	10.7/10.2	0.04	87.4
1.88 [0.18 KF]	2.4	0.05	55.5	0.6	3.2	0.05	80.0	10.4/10.2	0.05	86.9	10.9/10.3	-	87.4
				1.0	3.4	0.07	83.0	10.5/10.3	0.25	88.6	10.9/10.3	-	88.8
2.08 [0.20 KF]	2.3	0.06	55.7	0.6	3.7	0.04	80.7	10.4/10.0	0.06	87.1	10.8/10.3	0.02	88.0
				1.0	3.4	0.19	83.3	10.4/9.9	0.12	88.6	10.7/10.2	0.02	89.3

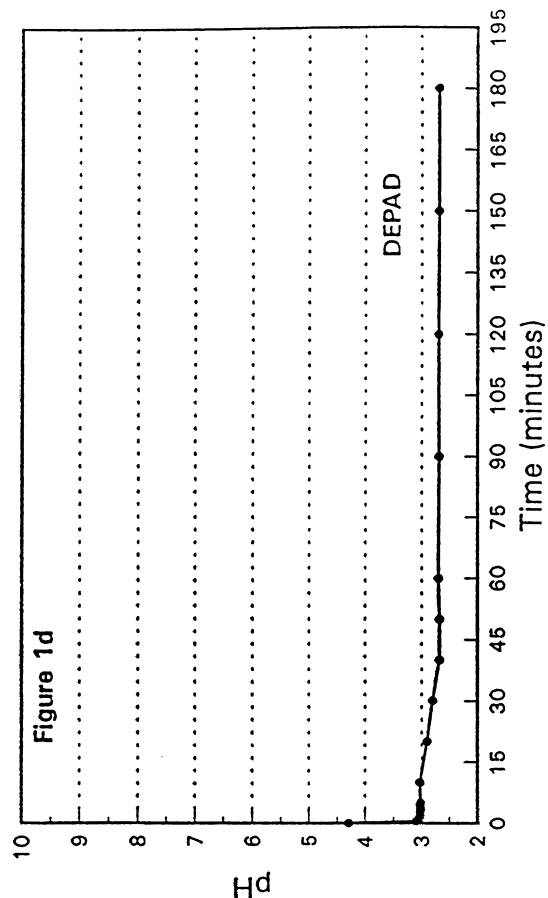
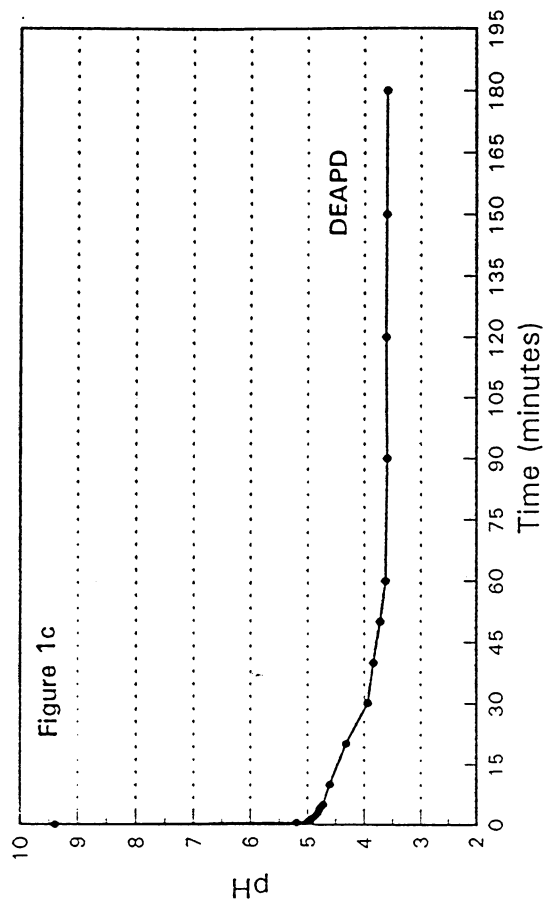
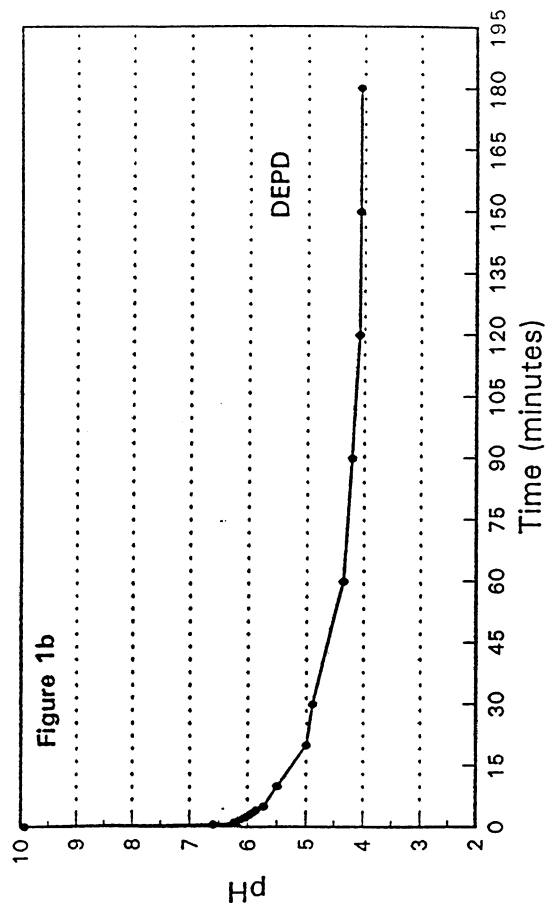
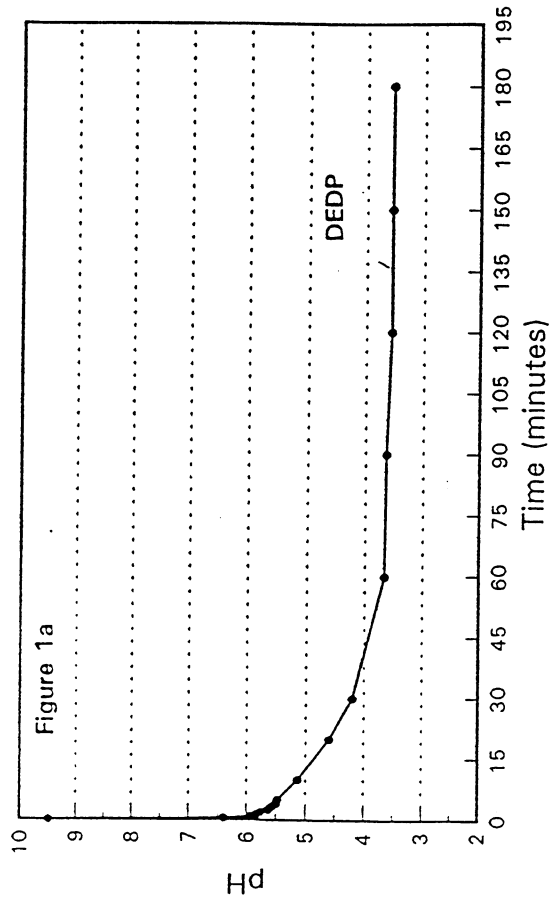
KF = Kappa factor
E = Caustic soda extractions
P = Hydrogen peroxide

TABLE 2a
DEPD AND DEDP BLEACHING OF NORTHERN
SOFTWOOD KRAFT PULP

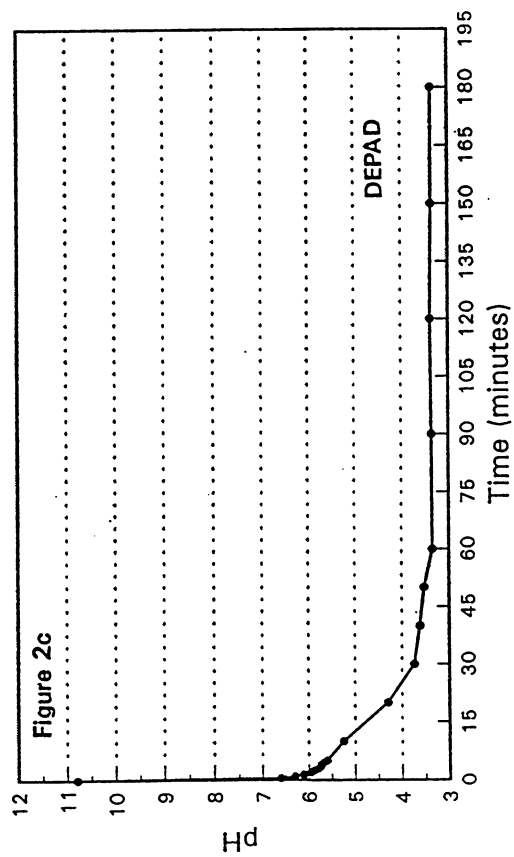
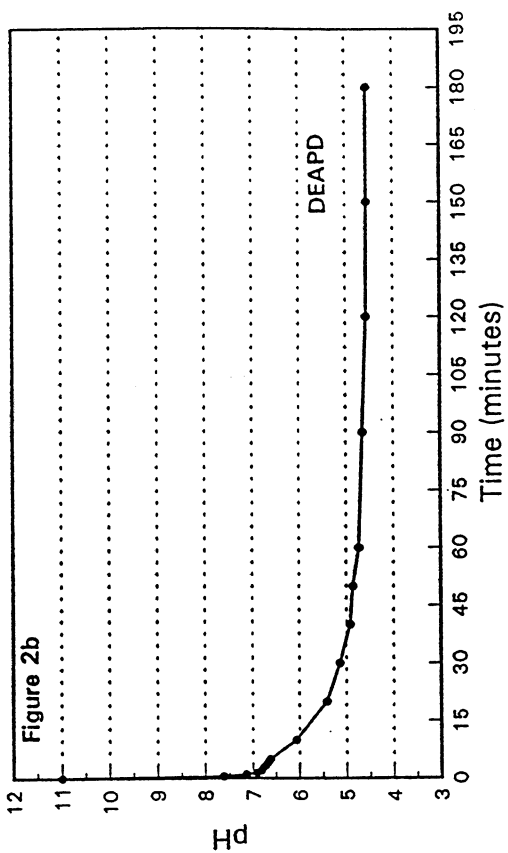
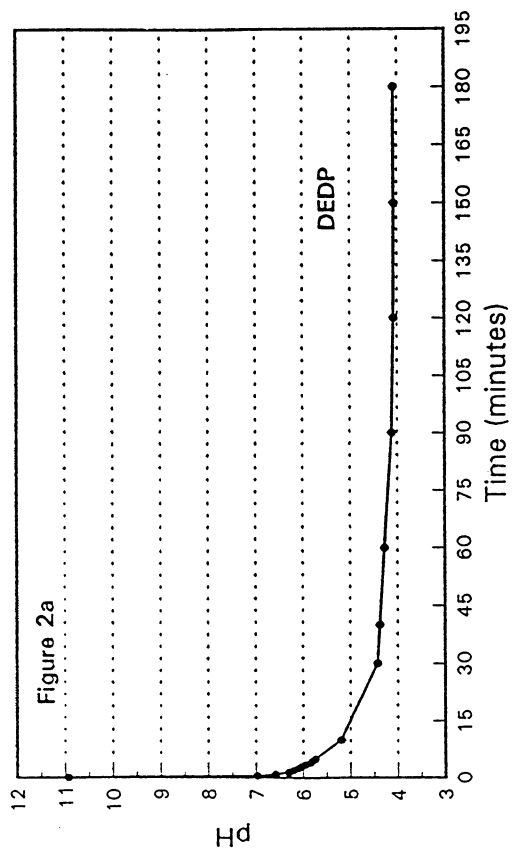
<i>DEPD Sequence</i>							
DE 1.82% ClO ₂ , 2.5% NaOH				2% H ₂ O ₂ 0.05% MgSO ₄ 0.8% NaOH		1.2% ClO ₂ 0.3% NaOH	
D Exit pH	DE pH in/out	DE Kappa #	DE Brightness (% ISO)	P-Stage pH in/out	P-Stage Brightness (% ISO)	D-Stage Exit pH	D-Stage Brightness (% ISO)
2.4	11.2/11.1	9.4	43.2	10.7/9.8	64.8	3.2	83.8
<i>DEAPD Sequence</i>							
2.6	11.2/11.0	9.4	46.1	10.9/10.0	66.5	2.9	83.9
<i>DEPAD Sequence</i>							
2.6	11.2/11.0	9.4	46.1	11.2/10.4	65.2	2.9	84.6
<i>DEDP Sequence</i>							
D Exit pH	DE pH in/out	DE Kappa #	DE Brightness (% ISO)	D ₁ -Stage Exit pH	D ₁ -Stage Brightness (% ISO)	P-Stage pH in/out	P-Stage Brightness (% ISO)
2.4	11.2/11.1	9.4	43.2	3.4	72.4	10.8/10.0	84.7

TABLE 2b
BLEACHING OF HARDWOOD KRAFT PULP

<i>DEPD Sequence</i>							
DE 0.47% ClO ₂ , 2% NaOH				2% H ₂ O ₂ 0.05% MgSO ₄ 0.9% NaOH		1.2% ClO ₂ 0.1% NaOH	
D Exit pH	DE pH in/out	DE Kappa #	Brightness (% ISO)	P-Stage pH in/out	P-Stage Brightness (% ISO)	D-Stage Exit pH	D-Stage Brightness (% ISO)
3.2	11.0/10.9	7.7	55.6	10.8/10.0	70.3	3.9	84.2
<i>DEAPD Sequence</i>							
2.8	11.0/10.6	7.7	57.0	10.7/9.9	69.6	2.7	83.0
<i>DEPAD Sequence</i>							
2.8	11.0/10.6	7.7	56.1	11.0/10.2	71.2	2.5	84.0
<i>DEDP Sequence</i>							
D Exit pH	DE pH in/out	DE Kappa #	DE Brightness (% ISO)	D-Stage Exit pH	D-Stage Brightness (% ISO)	P-Stage pH in/out	P-Stage Brightness (% ISO)
2.9	11.2/11.1	7.7	55.8	3.9	80.3	11.0/10.6	87.6



Figures 1a-d: Variation of pH during course of D_1 stage for hardwood pulp. The pH drop after the addition of the D_1 ClO_2 charge was measured at timed intervals for the sequences: DEDP (Fig. 1a); DEPD (Fig. 1b); DEAPD (Fig. 1c); DEPAD (Fig. 1d)



Figures 2 a-c: Variation of pH during course of D_1 stage during bleaching of softwood pulp. The pH drop after the addition of the D_1 ClO_2 charge was measured at timed intervals for the sequences: DEDP (Fig. 2a); DEAPD (Fig. 2b); DEPAD (Fig. 2c)

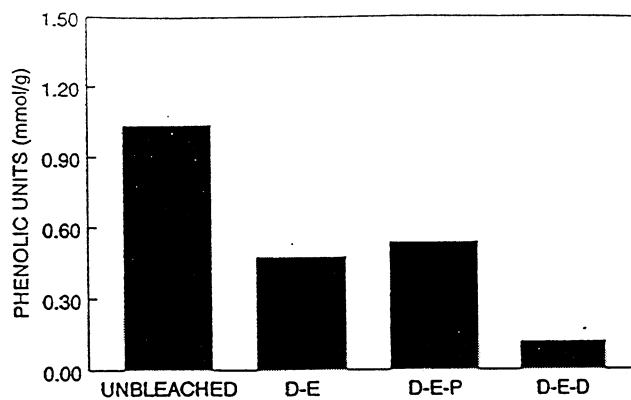


Figure 3a. Phenolic content of Northern softwood pulp by ^{31}P NMR

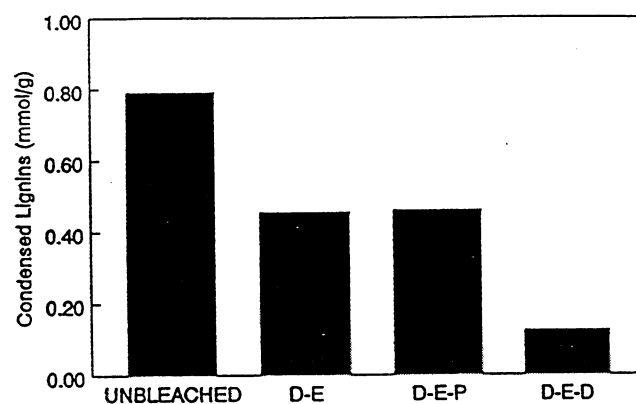


Figure 3b. Condensed lignin content of Northern softwood pulp by ^{31}P NMR

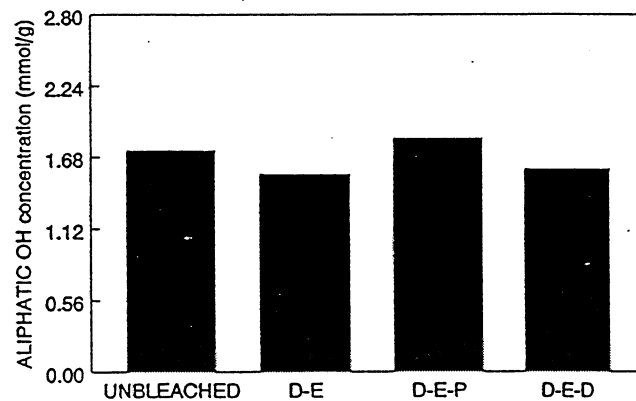


Figure 3c. Aliphatic hydroxyl content of Northern softwood pulp by ^{31}P NMR

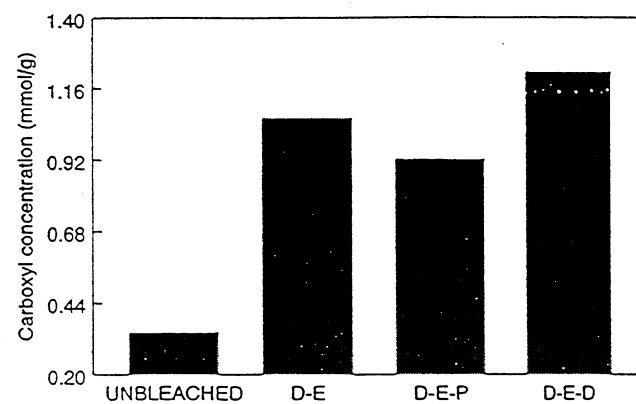


Figure 3d. Carboxyl concentration of Northern softwood pulp by ^{31}P NMR.

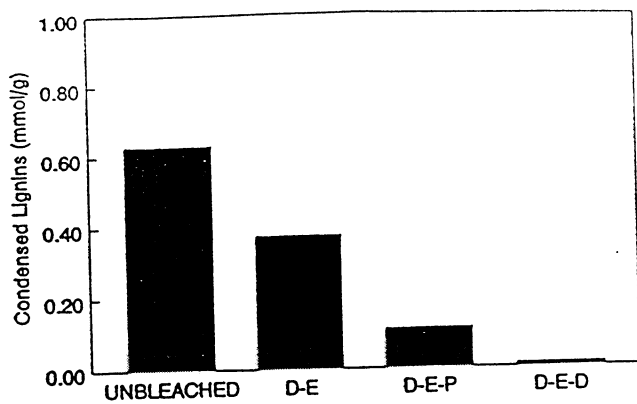


Figure 4a. Condensed lignin content of hardwood pulp by ^{31}P NMR.

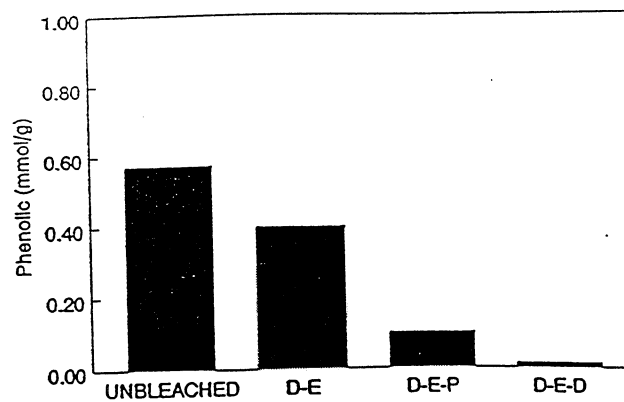


Figure 4b. Guaiacyl and demethylated phenolic content of hardwood pulp by ^{31}P NMR

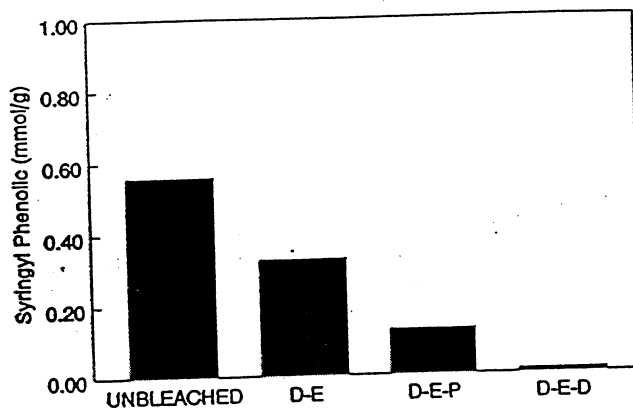


Figure 4c. Syringyl phenolic content of hardwood pulp by ^{31}P NMR.

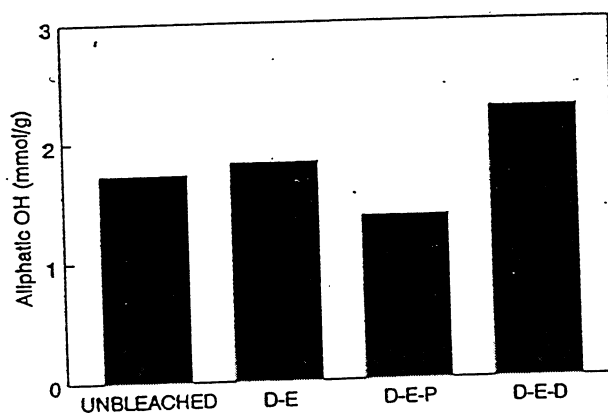


Figure 4d. Aliphatic hydroxyl concentration of hardwood pulp by ^{31}P NMR.

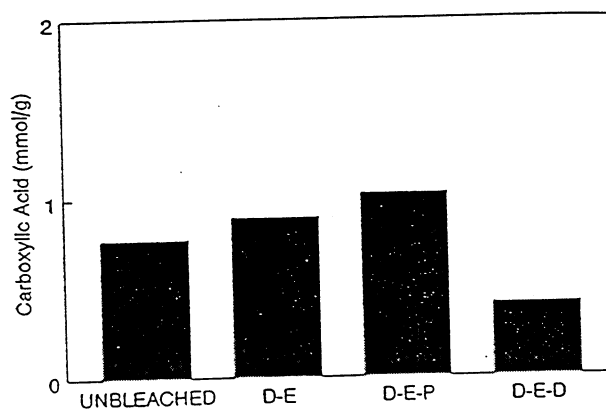


Figure 4e. Carboxylic acid concentration of hardwood pulp by ^{31}P NMR

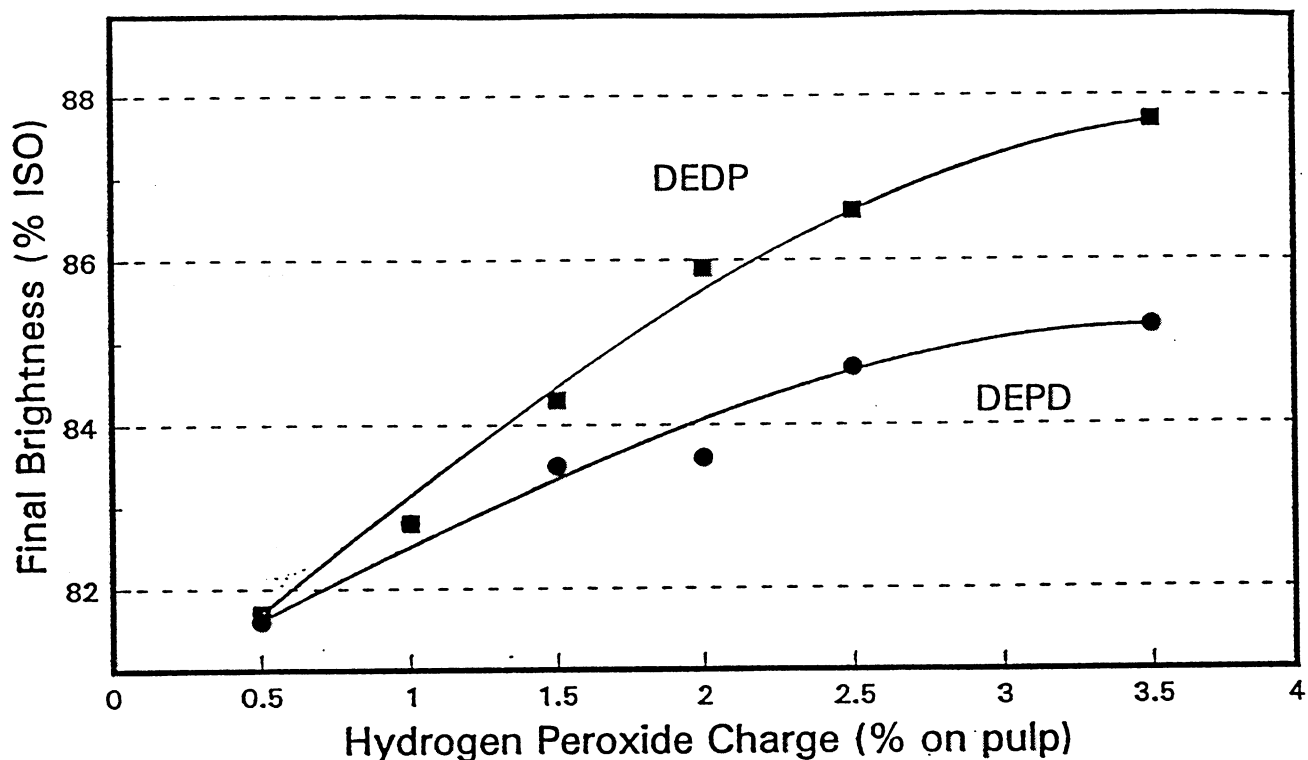


Figure 5. Effect of variation in P-stage charge on final brightness of softwood pulp bleached with DEDP and DEPD sequences.

TABLE 3
IRON MANGANESE CONTENT OF
ACID-WASHED PULPS

Pulp	Manganese (ppm)	Iron (ppm)
Softwood* Brownstock	114.4 ± 2.4	50.76 ± 0.39
Softwood DE	9.85 ± 1.11	49.80 ± 0.64
Softwood DEA	3.78 ± 0.81	40.26 ± 1.47
Hardwood Brownstock	30.08 ± 0.05	43.00 ± 2.29
Hardwood DE	1.85 ± 0.04	47.98 ± 8.88
Hardwood DEA	0.51 ± 0.09	38.77 ± 4.42

* Northern Softwood

